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December 1958

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Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

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RESEARCH ON NOVOCAIN THERAPY IN OLD AGE

American researchers and physicians can now judge for themselves the significance of the dramatic results of novocain therapy in maladies of old age, as reported by Dr. Anna Aslan, *Director of the Institute of Geriatrics, Bucharest, Rumania,* and her co-workers.

These seven papers, now in complete English translation, originally appeared in the West German journal *"Die Therapiewoche."* The authors report the results of large-scale clinical application of novocain injections for treatment of the sequelae of old age. The research has continued over a seven-year period and has covered more than 5,000 people. Dr. Aslan and her colleagues claim to have achieved a reversal of phenomena previously considered irreversible, e.g., in *cerebral arteriosclerosis;* they report sustained improvement in senile Parkinsonism, ichthyosis and senile keratosis, and a reduction in arteriosclerotic symptoms.

These reports have been translated and published in English so that they can be more readily subjected to objective analysis and evaluation by qualified scientists and physicians.

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A New Method for Prophylaxis and Treatment of Aging with Novocain—Eutrophic and Rejuvenating Effects • Prevention and Treatment of Diseases of the Aged—Views Concerning Treatment of Old Age • Biochemical and Physiological Criteria of Aging and Effects Thereon by Treatment, as a Measure of Rehabilitation • Recent Experiences on the Rejuvenating Effect of Novocain Together with Experimental, Clinical and Statistical Proof • Results of Treatment with Novocain in Dysmetabolic Arthropathies • Significance of Biomorphosis for Aging, Disease and Rejuvenation • First Experiences with Novocain Therapy of Old People.

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ALEKSEI ALEKSANDROVICH BALANDIN

Dear Aleksei Aleksandrovich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, congratulate you on the attainment of your sixtieth birthday.

Your investigations on catalysis and catalysis kinetics and your multiplet theory are known to an extremely wide circle of chemists. The results of your investigations have given us a deeper understanding of catalytic phenomena and have formed the basis of industrial chemical processes.

We wish you good health and further progress in your work.

Division of Chemical Science of the Academy of Sciences of the USSR

and

Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 16. SOLUBILITY ISOTHERMS OF THE TERNARY SYSTEM $Sr(OH)_2-H_2O_2-H_2O$

S. Z. Makarov and T. I. Arnol'd

The following peroxy compounds of strontium have been reported in the literature: SrO_2, $SrO_2 \cdot 8H_2O$, $SrO_2 \cdot 2H_2O_2$. There are only isolated references to the compounds $SrO_2 \cdot 6H_2O$ and $SrO_2 \cdot 0.5H_2O_2$. The principal method for the preparation of SrO_2 is that described by Thenard [1], by Riesenfeld and Nottebohm [2], and by Schöne [3, 4]. It consists in the treatment of strontium hydroxide with aqueous hydrogen peroxide solutions in presence of ammonia, or the action of sodium peroxide on aqueous strontium hydroxide.

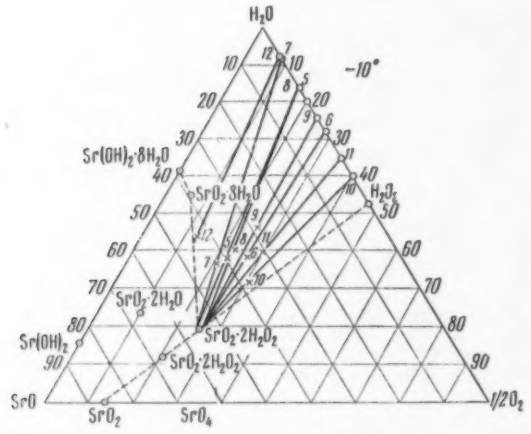

Fig. 1. 10° isotherm of the system $Sr(OH)_2-H_2O_2-H_2O$

All the methods described by Pirs [5] and by Centnerschwer and Blumenthal [6] are based on the formation of strontium peroxide by the oxidation of SrO or an amalgam with oxygen under pressure. These methods are not satisfactory because of the low yields of product. The use of ozone as oxidizing agent did not give good results either; the product contained not more than 1.03% of active oxygen. In a British patent Bergius [7] recommends that strontium oxide be fused with alkali or dissolved in ammonia or in an indifferent solvent; the resulting mixture is then treated with oxygen. After the oxidation the alkali can be dissolved out with alcohol, and the strontium peroxide is then left in a pure state. The electrolytic methods proposed by Nogareda [8] are just as ineffective.

Hence, the work reported in literature on the formation of strontium peroxide is solely of preparative interest. The inadequacy and unreliability of some of the data on the synthesis of SrO_2 quite naturally prompts the systematic investigation of the conditions under which strontium hydroxide reacts with hydrogen peroxide.

EXPERIMENTAL

In the investigation of the system $Sr(OH)_2-H_2O_2-H_2O$ our starting materials were solutions of pure hydrogen peroxide free from stabilizer and having concentrations of 0.5-97% and chemicallly pure $Sr(OH)_2$ recrystallized twice in a stream of nitrogen and free from carbonate. Equilibrium in the solutions was established under isothermal conditions in the course of three hours in a thermostat consisting of a 1-liter Dewar vessel mounted in a 10-liter Dewar vessel. In this thermostat it was possible to maintain a temperature within the required limits for four hours accurately within ± 0.2°. Cooling to the necessary temperature was effected with water, for +10°, with water and ice, for 0°, and with a 3:7 mixture of KCl and ice, for −10°. The time required for the attainment of equilibrium was established for each separate temperature by chemical analysis and by a graphical procedure from the constancy of the active-oxygen content of the liquid phase and the lack of change in the composition of the quilibrium solid phase. The time required did not usually exceed three hours. Samples were taken with

TABLE 1

Solubility Data for the System $Sr(OH)_2-H_2O_2-H_2O$ at −10°

Point No.	Composition of liquid phase (% by weight)				Composition of residue (% by weight)			Composition of solid phases
	1/2 O_2	H_2O_2	SrO	H_2O	1/2 O_2	SrO	H_2O	
17	7,95	16,79	0,10	91,95	13,20	43,80	43,00	Transitional (ice)
7	9,00	19,12	0,25	90,75	21,50	43,00	35,00	$SrO_2 \cdot 2H_2O_2$
5	16,50	35,06	0,20	83,30	22,50	38,50	39,00	Ditto
8	16,60	35,27	0,22	83,10	24,80	29,20	46,00	»
9	24,10	51,21	0,23	75,67	27,10	35,00	37,90	»
6	27,90	59,29	0,28	71,82	29,60	36,60	33,80	»
11	35,60	75,65	0,30	64,10	29,65	31,25	39,10	»
10	40,80	86,71	0,25	58,95	31,55	38,78	29,67	»

TABLE 2

Solubility Data for the System $Sr(OH)_2-H_2O_2-H_2O$ at 0°

Point No	Composition of liquid phase (% by weightt)				Composition of residue (% by weight)			Composition of solid phases
	1/2 O_2	H_2O_2	SrO	H_2O	1/2 O_2	SrO	H_2O	
20	0,16	0,34	0,0	99,84	1,60	30,30	68,10	$Sr(OH)_2 \cdot 8H_2O + SrO_2 \cdot 8H_2O$
27	0,30	0,64	0,12	99,58	3,69	33,00	63,31	$SrO_2 \cdot 8H_2O$
19	0,77	1,64	0,01	99,22	3,84	31,10	65,06	Ditto
12	0,85	1,81	0,05	99,10	4,45	32,46	63,09	» »
31	4,80	10,20	0,20	95,00	6,60	32,68	60,72	$SrO_2 \cdot 8H_2O + SrO_2 \cdot 2H_2O_2$
25	7,40	15,73	0,13	92,47	23,40	48,43	28,17	$SrO_2 \cdot 2H_2O_2$
8	8,31	17,66	0,13	91,56	24,50	54,00	21,50	Ditto
32	15,51	32,96	0,19	84,30	25,60	43,50	30,90	»
33	35,40	75,22	0,23	64,37	28,80	39,80	31,30	»
11	40,55	86,17	0,22	59,23	29,17	41,20	29,63	»

TABLE 3

Solubility Data for the System $Sr(OH)_2-H_2O_2-H_2O$ at 20°

Point No.	Composition of liquid phase (% by weight)				Composition of residue (% by weight)			Composition of solid phases
	1/2 O_2	H_2O_2	SrO	H_2O	1/2 O_2	SrO	H_2O	
16	0,34	0,72	0,06	99,60	2,66	30,50	66,84	$Sr(OH)_2 \cdot 8H_2O + SrO_2 \cdot 8H_2O$
12	0,68	1,44	0,063	99,26	5,75	34,50	59,75	$SrO_2 \cdot 8H_2O$
1	2,80	5,95	0,18	97,02	5,85	32,80	61,35	Ditto
6	2,90	6,16	0,22	96,88	7,24	33,30	59,46	$SrO_2 \cdot 8H_2O + SrO_2 \cdot 2H_2O_2$
18	20,80	44,20	0,20	79,00	23,90	39,20	36,90	$SrO_2 \cdot 2H_2O_2$
17	33,40	70,97	0,20	66,40	27,60	44,50	27,90	Ditto
19	42,70	90,74	0,17	57,13	30,80	37,80	31,40	»

the aid of a vessel consisting of a test tube with a side tube in which was placed a rubber stopper carrying a Schott No. 3 funnel protected from the CO_2 of the air. All this was placed in the Dewar flask containing the cooling mixture, so that filtration was carried out at the temperature of the experiment.

The composition of the solid phases were determined analytically and graphically by the method of residues. The results of chemical analysis on the residues and liquid phases were calculated as percent by weight of SrO, 1/2 O_2, and were plotted on Gibbs' triangles. The compositions of the liquid phases and residues were plotted on Gibbs' triangles. The compositions of the liquid phases and residues were determined analytically.

TABLE 4

Solubility Data for the System $Sr(OH)_2-H_2O_2-H_2O$ at 30°

Point No.	Composition of liquid phase (% by weight)				Composition of residue (% by weight)			Composition of solid phases
	1/2 O_2	H_2O_2	SrO	H_2O	1/2 O_2	SrO	H_2O	
18	0,18	0,38	0,04	99,78	1,70	30,00	68,30	$Sr(OH)_2 \cdot 8H_2O + SrO_2 \cdot 8H_2O$
17	0,29	0,62	0,06	99,65	5,10	31,70	63,20	$SrO_2 \cdot 8H_2O$
8	0,76	1,61	0,05	99,19	5,90	37,10	57,00	Ditto
14	1,10	2,34	—	98,90	6,10	32,10	61,80	»
11	2,16	4,59	0,13	97,71	6,10	32,10	61,80	»
16	2,20	4,67	0,21	97,59	16,20	40,00	43,80	»
1	2,20	4,67	0,22	97,58	16,20	44,60	39,20	$SrO_2 \cdot 8H_2O + SrO_2 \cdot 2H_2O_2$
5	13,87	29,47	0,19	85,94	21,00	40,00	39,00	$SrO_2 \cdot 2H_2O_2$
6	20,80	44,20	0,21	78,99	22,60	39,41	37,99	Ditto
10	38,30	81,39	0,16	61,54	25,20	37,60	37,20	»

TABLE 5

Solubility Data for the System $Sr(OH)_2-H_2O_2-H_2O$ at 50°

Point No.	Composition of liquid phase (% by weight)				Composition of residue (% by weight)			Composition of solid phases
	1/2 O_2	H_2O_2	SrO	H_2O	1/2 O_2	SrO	H_2O	
4	следы	следы	0,45	99,55	1,77	21,73	76,50	$Sr(OH)_2 \cdot 8H_2O + SrO_2 \cdot 8H_2O$
14	0,80	1,70	0,28	98,92	4,19	29,40	66,41	$SrO_2 \cdot 8H_2O$
15	0,95	2,02	0,27	98,78	4,50	30,30	65,20	Ditto
5	1,36	2,89	0,14	98,50	12,67	43,95	43,38	$SrO_2 \cdot H_2O_2$
3	2,50	5,31	0,17	97,33	13,29	52,93	33,78	Ditto
21	3,57	7,58	0,11	96,32	14,90	49,30	35,80	»
2	4,27	9,07	0,18	95,55	16,30	53,90	29,80	»
6	5,88	12,49	0,20	93,92	19,60	50,00	30,40	$SrO_2 \cdot H_2O_2 + SrO_2 \cdot 2H_2O_2$
16	6,10	12,96	0,17	93,73	20,80	41,46	37,74	$SrO_2 \cdot 2H_2O_2$
8	6,70	14,24	0,17	93,13	20,90	42,10	37,00	Ditto
10	8,50	18,06	0,17	91,33	22,00	47,00	33,00	»
12	12,00	25,50	0,23	87,77	23,00	48,60	28,40	»
11	18,70	39,74	0,28	81,02	23,75	37,09	39,16	»
7	22,30	47,39	0,21	77,49	23,80	40,82	35,38	»
13	30,25	64,28	0,23	69,52	27,40	34,95	37,65	»
9	42,48	90,27	0,20	57,32	32,10	33,30	34,60	»

Active oxygen was determined by titration with 0.1 N $KMnO_4$, and Sr was determined gravimetrically as $SrSO_4$.

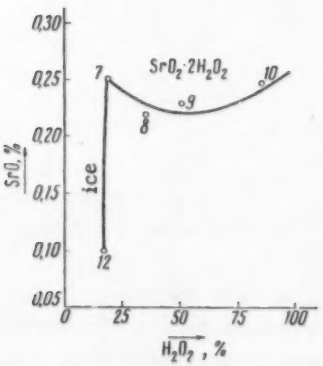

Fig. 2. Relation of SrO content of liquid phase at −10° to the H_2O_2 concentration.

Solubility Isotherms of the Ternary System $Sr(OH)_2-H_2O_2-H_2O$. The results obtained in the study of the −10°, 0°, 20°, 30°, and 50° solubility isotherms of the system $Sr(OH)_2-H_2O_2-H_2O$ are given in Tables 1-5 and are presented graphically in Figures 1, 3, 5, 7 and 9. At the same time graphs were plotted in rectangular coordinates, in which the abscissae were H_2O_2 contents and the ordinates were SrO contents in percent by weight (Figures 2, 4, 6, 8, and 10).

The −10° isotherm is limited by the region of frozen solutions in the H_2O_2 concentration range 0-16.8% and is characterized by the presence of one solid phase $SrO_2 \cdot 2H_2O_2$. The solid phase $SrO_2 \cdot 8H_2O$ is absent.

The 0°, 20°, and 30° isotherms are made up of branches corresponding to the solid phases $Sr(OH)_2$, $SrO_2 \cdot 8H_2O$, and $SrO_2 \cdot 2H_2O_2$. For all the temperatures studied the ranges of existence of $SrO_2 \cdot 8H_2O$ lie from 0% to the following limiting H_2O_2 concentration in the liquid phase;

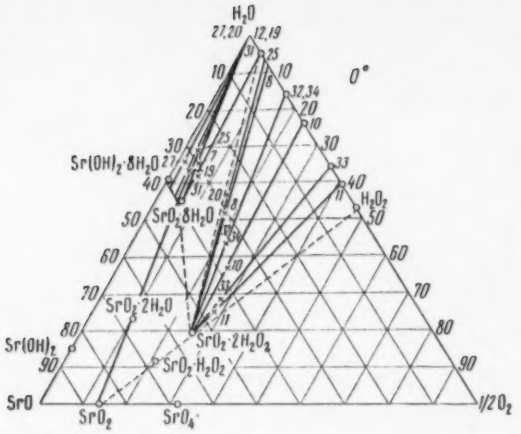

Fig. 3. 0° isotherm of the system $Sr(OH)_2-H_2O_2-H_2O$

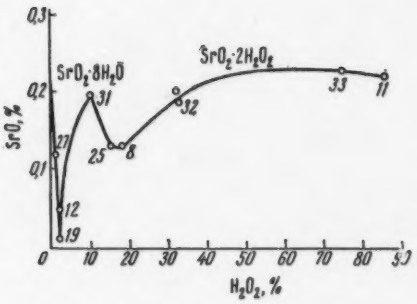

Fig. 4. Relation of SrO content of liquid phase at 0° to the H_2O_2 concentration.

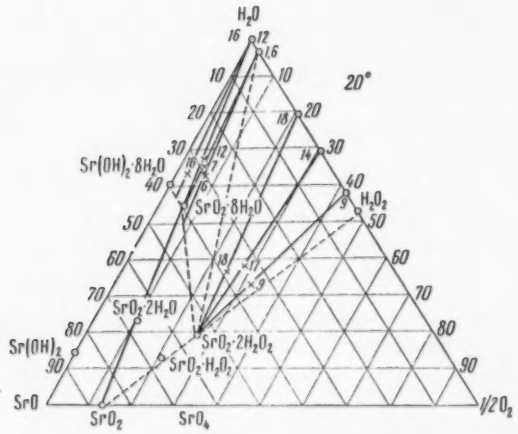

Fig. 5. 20° isotherm of the system $Sr(OH)_2-H_2O_2-H_2O$

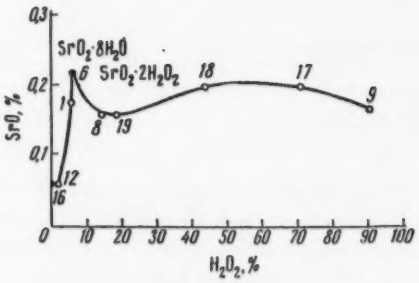

Fig. 6. Relation of SrO content of liquid phase at 20° to the H_2O_2 concentration.

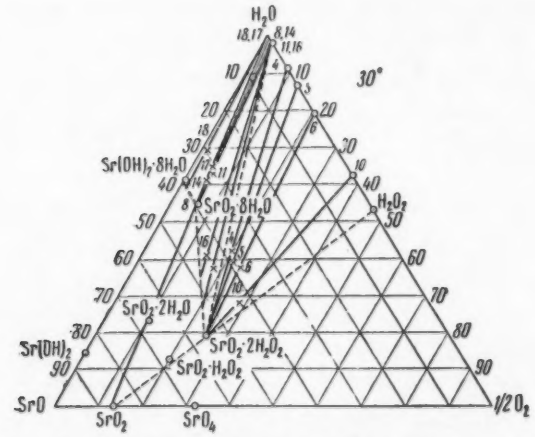

Fig. 7. 30° isotherm of the system $Sr(OH)_2-H_2O-H_2O$

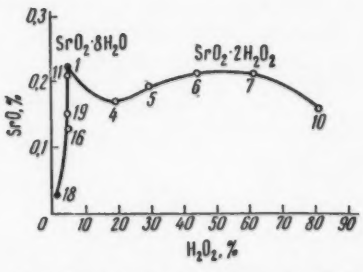

Fig. 8. Relation of SrO content of liquid phase at 30° to the H_2O_2 concentration.

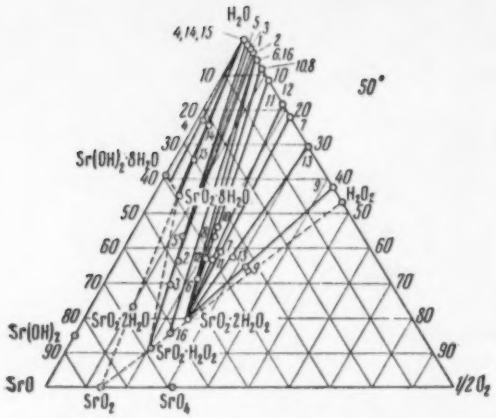

Fig. 9. 50° isotherm of the system $Sr(OH)_2-H_2O_2-H_2O$

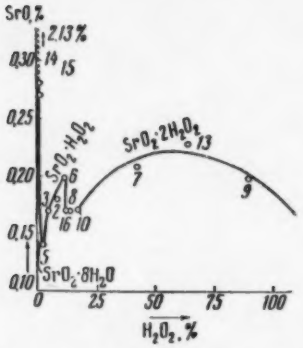

Fig. 10. Relation of SrO content of liquid phase at 50° to the H_2O_2 concentration

	−10°	0°	20°	30°	50°
H_2O_2 concentration in the liquid phase (% by weight)	0	10.2	6.16	4.67	2.02

For all the temperatures studied the ranges of existence of the solid phase $SrO_2 \cdot 2H_2O_2$ lie within the following limits of H_2O_2 concentration in the liquid phase:

	−10°	0°	20°	30°	50°
H_2O_2 concentration in the liquid phase (% by weight)	16.8-86.7	10.2-86.2	6.2-90.7	4.67-81.4	13.00-90.3

Study of the 50° isotherm revealed the existence of the compound $SrO_2 \cdot H_2O_2$, as well as the solid phases $SrO_2 \cdot 8H_2O$ and $SrO_2 \cdot 2H_2O_2$. This compound has not been reported previously in the literature; it exists at H_2O_2 concentrations in the liquid phase in the range 2.9-9.0%.

The diagrams obtained show that with rise in temperature from −10° to 50° the field of existence of $SrO_2 \cdot 2H_2O_2$ becomes smaller; at −10° strontium peroxide octahydrate does not exist, and at 0° it exists at hydrogen peroxide concentrations of up to 10.2%. At 30° this compound exists over a narrower range of H_2O_2 concentrations (0-4.67% in the liquid phase). The presence of strontium peroxide monoperhydrate $SrO_2 \cdot H_2O_2$ was established only at 50° at H_2O_2 concentrations in the liquid phase in the range 2.9-9.0%.

SUMMARY

1. The interaction between $Sr(OH)_2$ and H_2O_2 was investigated at various H_2O_2 concentrations by the solubility method in the system $Sr(OH)_2-H_2O_2-H_2O$ at −10°, 0°, 20°, 30° and 50°.

2. Compounds established with certainty by the method of residues were strontium peroxide octahydrate $SrO_2 \cdot 8H_2$ and strontium peroxide diperhydrate $SrO_2 \cdot 2H_2O_2$. The existence was established of the previously unknown strontium peroxide monoperhydrate $SrO_2 \cdot H_2O_2$, which is stable at H_2O_2 concentrations in the liquid phase from 2.9% to 9.0% at 50°.

3. Data in the literature on the existence of semi- and hexa-hydrates were not confirmed. The only hydrate form is strontium peroxide octahydrate $SrO_2 \cdot 8H_2O$.

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PHYSICAL CHEMISTRY

RELATION BETWEEN THE CATALYTIC ACTIVITY OF BINARY COMPOUNDS OF GROUP II METALS WITH NONMETALS AND THE POSITIONS OF THE ELEMENTS IN MENDELEEV'S PERIODIC SYSTEM

COMMUNICATION 4. CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL OVER ZINC SELENIDE AND TELLURIDE

O. V. Krylov, M. Ia. Kushnerev, and E. A. Fokina

In this paper we report an investigation of the catalytic activity of selenides and tellurides of Group II metals in the dehydrogenation and dehydration of isopropyl alcohol; it continues our investigations on the oxides and sulfides of metals of this group [1-3].

EXPERIMENTAL

The procedure used in the kinetic and adsorption investigations was described in previous papers [1-3]. A preparation of ZnSe was kindly made available by M. S. Belen'kii, who synthesized it by the "wet" method (precipitation of ZnSe from solution with hydrogen selenide). A preparation of ZnTe was kindly supplied by N. A. Goriunova, who prepared it by fusing elementary Zn and Te together in stoichiometric amounts in a vacuum at a temperature above their melting points.

TABLE 1

Composition of Products of the Decomposition of Isopropyl Alcohol over ZnSe

Temperature (°C)	Pressure (mm) of reaction products after freezing treatment with			Composition (mm) of prod. on assumption of 2 parallel reactions		$2[H_2]+2[C_3H_6]$	Pressure of reaction products before freezing treatment (mm)
	liquid N_2	solid n-propyl alcohol	solid CO_2	$[H_2]=-[C_3H_6O]$	$[C_3H_6]=-[H_2O]$		
20	0,009		0,010	0,004	0,002	0,012	
50	0,050		0,143	0,050	0,043	0,186	0,170
85	0,280	0,337		0,280	0,057	0,674	0,710
100	0,310	0,331		0,310	0,021	0,662	~1
120	0,364	0,387		0,364	0,023	0,774	~1
140	0,610	0,625		0,610	0,015	1,250	>1
100	0,305	0,331		0,305	0,027	0,662	0,826
50	0,018	0,032	0,056	0,018	0,014	0,064	0,062
120	0,264	0,315		0,264	0,051	0,630	~1

The specific surface of the ZnSe, measured by adsorption of n-heptane and calculated from the BET equation, was 175 sq.m/g. The specific surface of the ZnTe was small, and adsorption on it could scarcely be measured on a McBain balance; it was of the order of 1 sq.m/g.

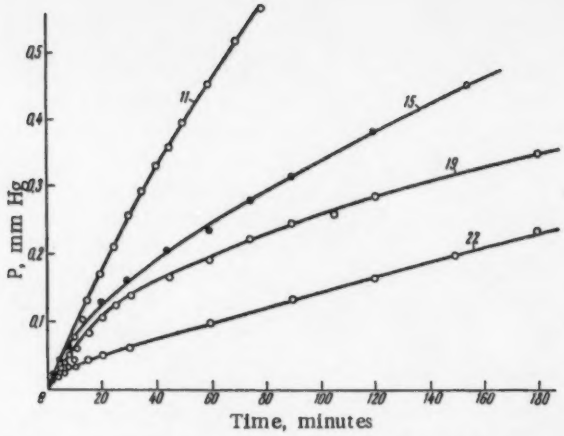

Fig. 1. Kinetic curves for the dehydrogenation of isopropyl alcohol in a layer adsorbed on ZnSe. The curves are numbered according to the serial number of the experiment, i.e. other experiments, not shown, were carried out after each of the experiments represented in Fig. 1.

Table 1 gives some experimental results on the decomposition of isopropyl alcohol on zinc selenide in the adsorbed layer. The preliminary adsorption of the alcohol was carried out for five minutes at room temperature; the excess of the alcohol remaining in the gas phase was then frozen out. The results showed that, under the given conditions, the decomposition of isopropyl alcohol on zinc selenide proceeds mainly in the direction of dehydrogenation. There may be some dehydration, generally to the extent of 10-20%, but in some experiments, e. g. some at 20°, decomposition proceeded entirely by dehydrogenation. It is notable that whereas below 100° the material balance of the decomposition reaction determined by the freezing-out method was quite satisfactory, above 100° the sum of the dehydrogenation and dehydration products was considerably below the pressure of the products before the freezing treatment. This indicates the desorption of some condensable products at high temperatures.

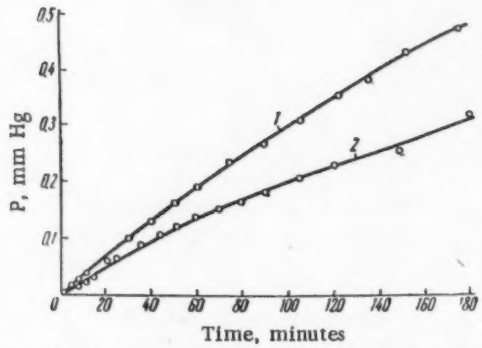

Fig. 2. Kinetic curves for the over-all decomposition (1) and dehydrogenation (2) of isopropyl alcohol in an adsorbed layer on ZnSe.

From the results in Table 1, which are arranged in order in which the experiments were done, it can be seen that after a series of experiments at a high temperature the character of the decomposition of the isopropyl alcohol changes considerably. At the same time there is a fall in reaction rate. Fig. 1 shows the kinetic curves for the dehydrogenation of isopropyl alcohol in the adsorbed layer at 120°. From Experiment 11 to Experiment 22 the reaction rate fell to about one-quarter of its original value. In the course of a single experiment there was little change in reaction rate, i. e. the order of reaction was close to zero. The greatest reduction in rate was observed in the initial part of the kinetic curve.

Fig. 2 gives kinetic curves for the over-all decomposition (1) and dehydrogenation (2) of isopropyl alcohol in the adsorption layer at 85° determined by freezing out reaction products with n-propyl alcohol in the first case and with liquid nitrogen in the second. Both curves are of low curvature, i. e., the order of the reaction is close to zero. The change in catalyst activity during the reaction did not permit the subtraction of the ordinates of Curve (2) from those of Curve (1) to give the kinetic curve for the dehydration of the alcohol, as was done in the investigation [3].

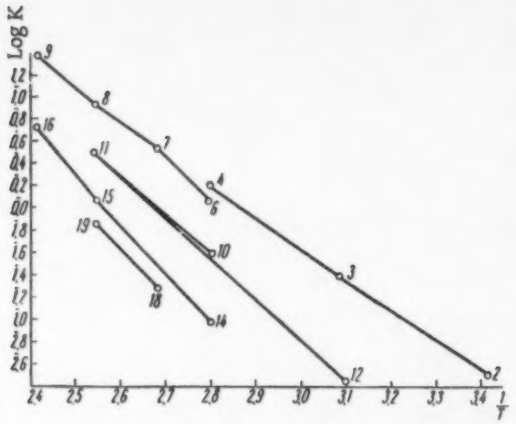

Fig. 3. Relation of log K to 1/T for the over-all decomposition (No. 2-9) and the dehydrogenation (No. 10-19) of isopropyl alcohol in an adsorbed layer on ZnSe. The numbers near the points are serial numbers of experiments.

In order to determine the possibility of obtaining the activation energy by the method described in a previous paper [3], we calculated the initial coverage of the ZnSe surface with adsorbed isopropyl alcohol. The results in Table 2 show that with change in temperature from 20° to 150° the surface coverage of the adsorbed alcohol changes relatively little, in comparison with the changes in the case of ZnO and ZnS. The closeness of the initial coverages and the comparatively small change in the activity of the ZnSe over two successive experiments made it possible to calculate the activation energy with the aid of values of rate constants obtained from the slopes of kinetic curves of two successive experiments at different temperatures. As the changes were generally made starting from lower temperatures and ending with higher, the resulting figures are somewhat too low, though not by more than 1-2 kcal. The corresponding Arrhenius straight lines are given in Fig. 3. The activation energies calculated in this way are given in Table 3.

These results show that reduction in the activity of the ZnSe is accompanied by increase in activation energy.

In view of the possible oxidation of the surface of the ZnSe in the course of the decomposition of the isopropyl alcohol [4] it was desirable to study this reaction on a previously oxidized sample. For this purpose a portion of the ZnSe was roasted for three hours in the air at 600°. Fig. 4 gives the kinetic curves for the dehydrogenation of isopropyl alcohol in the adsorbed layer on this sample with freezing-outof the reaction products with

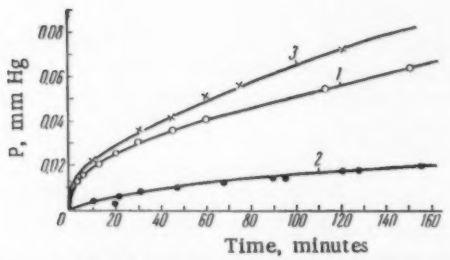

Fig. 4. Kinetic curves for the dehydrogenation of isopropyl alcohol in the adsorbed layer on a sample of ZnSe which had been roasted in the air at 600°:
1) 130°; 2) 85°; 3) 150°.

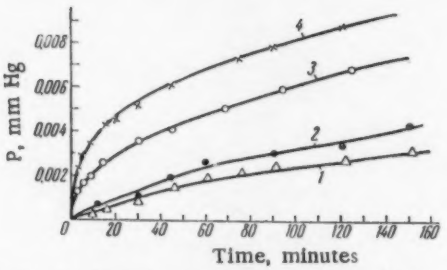

Fig. 5. Kinetic curves for the over-all decomposition of isopropyl alcohol in the adsorbed layer on a sample of ZnSe which had been roasted in the air at 600°:
1) 85°; 2) 100°; 3) 130°; 4) 150°.

TABLE 2

Surface Coverage of ZnSe in the Adsorption of Isopropyl Alcohol

Temperature (°C)	20	50	60	100	130	135	150
Coverage (%)	7.5	4.9	7.9	6.9	5.7	6.0	4.2

TABLE 3

Activation Energy for Over-all Decomposition (E_1) and Dehydrogenation (E_2) of Isopropyl Alcohol in an Adsorbed Layer on ZnSe.

Expetiment No.	2–3	3–4	6–7	7–8	8–9
E_1 in cal/mole	12200	13200	17400	13900	16200
Experiment No.	10–11	11–12	14–15	15–16	18–19
E_2 in cal/mole	15600	17000	20300	22600	21300

solid propyl alcohol. The reaction products, as could be judged by analysis by means of freezing treatments, consisted of dehydrogenation and dehydration products. In the decomposition of the alcohol, the activation energy for dehydrogenation, as determined from the curves in Fig. 4, increases from 20 to 24 kcal/mole, and the activation energy for the over-all decomposition, according to the curves in Fig. 5, increases from 16 to 21 kcal/mole.

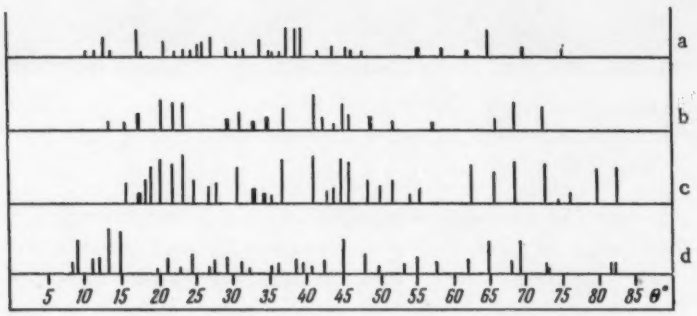

Fig. 6. X-ray diagrams of zinc selenide samples:
a) original sample; b) sample after use as catalyst; c) sample roasted in the air at 600°; d) deposit of SeO_2 on cold wall after roasting of ZnSe in the air.

Figures 6 and 7 show x-ray diagrams of the original (a), used (b), and roasted (c) samples of zinc selenide. The x-ray photographs were taken with $K\alpha_{1,2}$ iron radiation at 30 kilovolts in an x-ray camera having a diameter of 5.73 mm. Fig. 8 shows electron-diffraction pictures of zinc selenide samples taken in an EM-4 electronograph at a potentive of 40 kv.

The decomposition of isopropyl alcohol in an adsorbed layer of ZnTe proceeded at a considerable rate at 20°. The coverage of the ZnTe surface with adsorbed alcohol at 20° was about 15% (calculated for a surface of 1 sq.m). Fig. 9 gives kinetic curves for the over-all decomposition of isopropyl alcohol at the ZnTe surface at 20° and 50°. The fall in the reaction rate in the experiment at 50°, which was carried out after the experiment at 20°, demonstrates the great fall in catalytic activity during reaction. It was shown by freezing treatments that at 20° gaseous products contain 26% of dehydrogenation products and 34% of dehydration products, whereas at 50° they contain about equal amounts of dehydrogenation and dehydration products. Fig. 10 gives kinetic curves for the dehydrogenation of isopropyl alcohol in an adsorbed layer on ZnTe, i.e. with freezing out of products with liquid nitrogen. Fig. 11 gives a diagrammatic representation of the x-ray photographs of the original (a) and used (b) samples of zinc telluride.

Study of the catalytic properties of chemically pure tellurium provided by A. V. Novoselova, which had a somewhat greater specific surface than our sample of ZnTe, showed that the decomposition of the alcohol was small at 100° and was accompanied by poisoning of the surface, which after only 20–25 minutes led to complete loss of activity.

Fig. 7. X-ray photographs of samples of zinc selenide:
a) original sample; b) sample after use as catalyst.

Fig. 8. Electron-diffraction photographs of zinc selenide
a) original sample; b) sample after use as a catalyst; c) sample roasted in the air at 600°; d) deposit of SeO_2 on cold wall after roasting of ZnSe in the air.

Experiments on the acid-base properties of zinc selenide showed that at 28° ZnSe adsorbs 4.1 μmoles of phenol per sq.m of surface; after desorption at 28° there remains 0.7 μmole, and at 100° complete desorption occurs. At 25° 10.5 μmoles of pyridine is adsorbed; after desorption at 25° there remains 1.9 μmoles, at 100° there

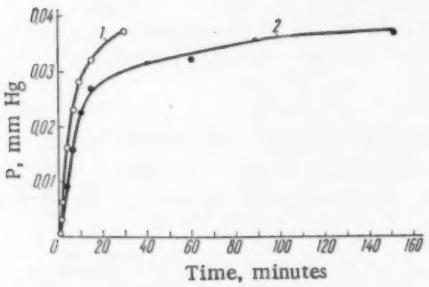

Fig. 9. Kinetic curves for the over-all decomposition of isopropyl alcohol in an adsorbed layer of ZnTe:
1) 20°; 2) 50°.

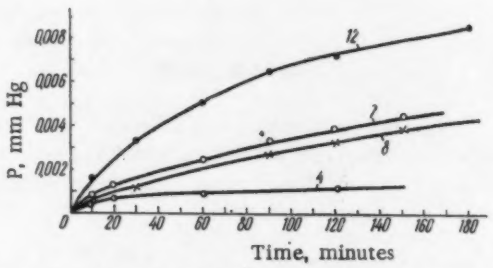

Fig. 10. Kinetic curves for the dehydrogenation of isopropyl alcohol in an adsorbed layer on ZnTe:
4) 50°; 8) 80°; 7) 100°; 12) 150°. The numbering of the curves corresponds to the serial numbering of the experiments.

remains 0.2 μmole, and at 150° desorption is complete. Zinc telluride had such a small specific surface that we were unable to investigate its acid-base properties by this method.

DISCUSSION OF EXPERIMENTAL RESULTS

The decomposition of isopropyl alcohol at low temperatures, at which the synthesis of alcohols occurs under

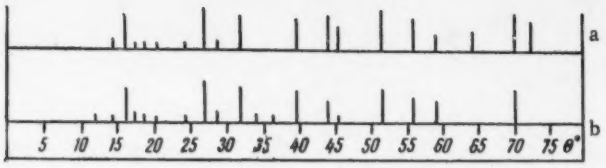

Fig. 11. X-ray diagrams of zinc telluride samples:
a) original; b) sample used as catalyst.

certain conditions, is not contrary to thermodynamics. Thus, the equation for the equilibrium constant for the hydration of propene

$$C_3H_6 + H_2O \rightleftarrows i\text{-}C_3H_7OH,$$

calculated from tables of standard heats of formation and entropy [5] has the form:

$$\lg K_p = \frac{3047}{T} - 7{,}39 - 1{,}07\,F\left(\frac{T}{298}\right).$$

This gives $K_p = 1.02 \cdot 10^3$ at 293°K. The equilibrium conversion of isopropyl alcohol into propene at 293°K is 57% at 1 mm, 89% at 0.1 mm, and 99% at 0.01 mm. The equilibrium constant for the dehydrogenation of isopropyl alcohol was measured experimentally by Stoddart and Kemball [6]. At 321°K $\log K_p = \bar{3}.5396$, and at 296°K $\log K_p = \bar{4}.3050$. Hence, at the low pressure realized in the decomposition of the alcohol in a layer the equilibrium is greatly displaced in the direction of dehydrogenation and dehydration of the alcohol.

We calculated changes in free energy [7] for the following reactions:*

$$ZnS + H_2O = ZnO + H_2S;\ \lg K_p = -\frac{4002}{T} + 0.162 \quad (1)$$

$$ZnSe + H_2O = ZnO + H_2Se;\ \lg K_p = -\frac{6365}{T} + 0{,}390 \quad (2)$$

$$ZnTe + H_2O = ZnO + H_2Te;\ \lg K_p = -\frac{8664}{T} + 0{,}538 \quad (3)$$

$$H_2 + ZnO = Zn + H_2O;\ \lg K_p = -\frac{12461}{T} + 7{,}8 \quad (4)$$

$$H_2 + ZnS = Zn + H_2S;\ \lg K_p = -\frac{16363}{T} + 9{,}307 \quad (5)$$

$$H_2 + ZnSe = Zn + H_2Se;\ \lg K_p = -18726/T + 9{,}536 \quad (6)$$

$$ZnO = Zn + {}^1/_2O_2;\ \lg K_p = -24991/T + 11{,}463 \quad (7)$$

$$ZnS = Zn + S;\ \lg K_p = -29035/T + 14{,}146 \quad (8)$$

$$ZnSe = Zn + Se;\ \lg K_p = -24816/T + 14{,}146 \quad (9)$$

$$ZnTe = Zn + Te;\ \lg K_p = -23773/T + 15{,}105 \quad (10)$$

$$ZnS + 2ZnO = 3Zn + SO_2;\ \lg K_p = -51890/T + 30{,}58 \quad (11)$$

$$ZnS + ZnSO_4 = 2Zn + 2SO_2;\ \lg K_p = -44326/T + 33{,}24 \quad (12)$$

$$ZnS + 3ZnSO_4 = 4ZnO + 4SO_2;\ \lg K_p = -7300/T + 9{,}40 \quad (13)$$

$$ZnS + \frac{3}{2}O_2 = ZnO + SO_2;\ \lg K_p = 23083/T - 3{,}80 \quad (14)$$

$$ZnS + 2O_2 = ZnSO_4;\ \lg K_p = 40513/T - 8{,}743 \quad (15)$$

* In the calculation of K_p, for ZnS we used values applying to sphalerite, for Zn in Equations (5)-(11) values applying to solid Zn, and for Zn in Equations (16)-(18) values applying to liquid Zn.

$$ZnTe + 2ZnO = 3Zn + TeO_2;\ \lg K_p = 26466/T + 1{,}72 \quad (16)$$

$$ZnO + C_3H_7OH = C_3H_6O + Zn + H_2O;\ \lg K_p = -8838/T + 8{,}78 \quad (17)$$

$$ZnS + C_3H_7OH = C_3H_6O + Zn + H_2S;\ \lg K_p = -12840/T + 8{,}942 \quad (18)$$

Examination of Equations (1)-(3) shows that the hydrolysis of ZnS, ZnSe, and ZnTe with formation of ZnO is not to be expected under catalysis conditions. Even in the case of ZnS this reaction begins to be appreciable only above 700°, and for ZnSe and ZnTe still higher temperatures are required. At room temperature the equilibrium is displaced in the other direction. The presence of ZnO in the catalyst after the reaction can be explained by reaction between ZnS and $ZnSO_4$ according to Equations (12) and (13) and by the analogous reactions of ZnSe and ZnTe. Thus, the equilibrium pressure of SO_2 formed by Reaction (13) at 200° is 0.001 mm, but at 400° it is 30 mm. The presence of $ZnSO_4$ and other oxidized forms of Zn, S, Se, and Te, formed in Reactions (14), (15), and others, is extremely likely in view of the fact that the catalyst spends a period in the air before it is introduced into the apparatus. The formation of metallic Zn By Reactions (4)-(12) and (16) is thermodynamically improbable at low temperatures (0-400°). However, the reduction of ZnO and ZnS (and also ZnSe and ZnTe) by alcohol [Reactions (17) and (18)] may occur at much lower temperatures. Thus, for Reaction (17) at 200° and at a pressure of 10^{-6} mm, $K_\gamma = K_p/p^2 = 10^{1}$ The possibility of the occurrence of Reaction (17) at low temperature is confirmed also by kinetic data [8]. Analogous reactions can lead to the formation of H_2Se and H_2Te, which may dissociate into their elements with rise in temperature and reduction in pressure.

The x-ray data (Figures 6 and 7) confirm the results of thermodynamic calculations. The original sample of zinc selenide gives a complex x-ray photograph in which some of the lines refer to cubic ZnSe with $\underline{a}$ = 5.668 A and some refer to tetragonal SeO_2 with $\underline{a}$ = 8.35 A and $\underline{c}$ = 5.05 A. Some of the lines could not be unequivocally identified but their character and relative positions indicated that they belonged to a crystalline phase of low degree of symmetry, possible the little-studied zinc selenate hydrate $ZnSeO_4 \cdot nH_2O$ [9], which has a syngony of low symmetry (monoclinic and triclinic). Moreover, the x-ray photograph showed great incoherent scattering at large reflection angles, which indicates the presence of strongly marked dislocation in one or several phases. Judging from the relative breadths of the lines, the dispersion of the original ZnSe phase was greater than that of the other phases in the original sample.

After the reaction the sample contained crystalline ZnSe and ZnO formed by a reaction analogous to Reaction (13):

$$3ZnSeO_4 \cdot nH_2O + ZnSe = 4ZnO + 4SeO_2 + 3nH_2O$$

The incoherent scattering was not weakened appreciably. Roasting in the air at 600° resulted in the formation of well crystallized ZnSe phases, and incoherent scattering disappeared. In both cases SeO_2 vaporized and was deposited on the cold wall of the apparatus.

The electron-diffraction data (Fig. 8) showed that on the surfaces of the original and used catalysts there was highly dispersed ZnSe with very little admixture of ZnO (a little more after the reaction). Roasting of the sample at 600° led to a considerable increase in the size of the crystals in the surface layer of ZnSe and ZnO, but the phase composition did not change. The average sizes of the ZnSe crystals calculated from the electron-diffraction diagrams were 40-50 A for the original and used samples and 110-120 A for the roasted samples.

Taking account of the like changes in the breadths of the ZnSe and ZnO lines and neglecting the differences introduced into the calculation of dispersion by the different types of lattice, we may determine the specific surfaces of the samples from the following equation [10], on the assumption that the surface is completely covered with zinc selenide:

$$S = \frac{1}{e} \cdot \frac{6}{d} \cdot 10^4 m^2/g$$

in which $\underline{e}$ is the size of the crystals as given by electron- or x-ray diffraction data and $\underline{d}$ is the true density of the substance. The subtitution of numerical values gives 250 sq.m/g for the original and used samples and 100 sq.m/g for the roasted sample; as would be expected, these are somewhat higher than the values determined by the BET equation from the adsorption of n-heptane (175 sq.m/g for the original sample).

The activation energy for dehydrogenation over a sample of zinc selenide roasted in the air is greater than for ZnSe (15-22 kcal/mole) and less than that for ZnO (25-46 kcal/mole). The activity of this sample is less than

that of the original zinc selenide. On the basis of these catalytic and x-ray data, it may be suggested that the decomposition of isopropyl alcohol over ZnSe does not in itself cause structural changes in the sample, and the observed chemical changes are due to impurities in the original sample and to the temperature conditions. The lowness of the activities of ZnO and of roasted ZnSe indicates that in the given case the catalytically active phase is indeed ZnSe.

Examination of the x-ray photographs of zinc telluride (Fig. 11) showed that the original and used samples did not differ substantially in phase composition and dispersion; they both contained cubic ZnTe with a lattice parameter of 6.07 A and a little TeO_2. A slight increase in the intensities of the diffraction lines of TeO_2 on the x-ray photograph of the used sample may be explained by its recrystallization under the action of heat. On the basis of these results, we may conclude that the decomposition of isopropyl alcohol proceeds over ZnTe without bringing about any changes in the x-ray structure of the catalyst. Pure tellurium is of low activity, and it is probable that in the case of zinc telluride, the active phase is ZnTe itself.

We take the opportunity of thanking M. S. Belen'kii and N. A. Goriunova for the provision of preparations.

SUMMARY

1. A study was made of the decomposition of isopropyl alcohol over ZnSe and ZnTe in the temperature range 20-140°. Reaction proceeds mainly in the direction of dehydrogenation.

2. There is a reduction of the catalytic activities of ZnSe and ZnTe during reaction. The activation energy for the dehydrogenation of the alcohol over ZnSe rises from 15 to 21 kcal/mole.

3. The activity of ZnSe is reduced by roasting it in air at 600°. Elementary tellurium has low catalytic activity.

4. Investigation by x-ray- and electron-diffraction methods, taken in conjunction with the thermodynamic characteristics, showed that the phase changes in the catalyst were due to impurities in the original sample and to the effect of temperature, and not to the occurrence of the catalytic reaction.

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RETARDATION OF THE OXIDATION OF FATS BY ASCORBIC ESTERS

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Edible fats, which are mixtures of triglycerides of saturated and unsaturated fatty acids, readily undergo oxidative deterioration in contact with air. The possibility of using antioxidants to increase the stability of edible fats to oxidation is of considerable interest. As antioxidants, extensive use is made of phenolic compounds: butylmethoxyphenol, butylcresol, nordihydroguaiaretic acid, and gallic esters. The effectiveness of phenolic antioxidants can be increased by the addition of synergistic antioxidants or synergists, e. g. certain amino acids and ascorbic acid and its derivatives, in particular the palmitic ester of ascorbic acid ("ascorbyl" palmitate).

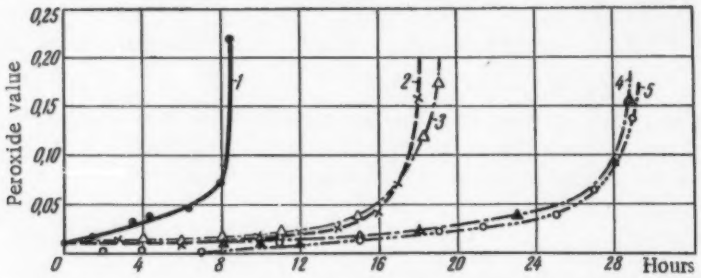
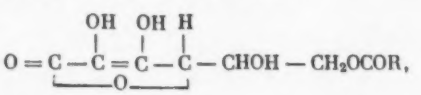


Fig. 1. Kinetic curves for the oxidation of lard with added ascorbic ester preparations:
1) without addition (control); 2) addition of 0.02% of ascorbyl palmitate (Preparation 1); 3) addition of 0.02% of ascorbyl palmitate (Preparation 2); 4) addition of 0.02 of ascorbyl palmitate (Preparation 3); 5) addition of 0.02% of an ascorbic ester preparation prepared from a mixture of synthetic fatty acids. Temperature of oxidation 100°.

The ability of ascorbic acid to restrain the development of oxidative processes has been demonstrated for a variety of systems. Thus, ascorbic acid has found application in the food industry as a restrainer of the oxidative changes of the pigments of muscle tissue and blood (myoglobin and hemoglobin) [1]. Gray and Stone [2] obtained a patent for a method of raising the stability of fat emulsions to oxidation by treating them with ascorbic acid and related substances. These authors [3] showed that ascorbic and D-glucoascorbic acid greatly retard the oxidation or fatty substances which were in contact with water. Golumbic and Matill [4] found that ascorbic acid itself, and, particularly, its mixture with tocopherol, is an effective inhibitor of the oxidation of lard. This indicates that ascorbic acid has synergistic properties. Calkins and Mattill [5] investigated the synergism of ascorbic acid with quinones in the stabilization of the ethyl esters of the fatty acids of lard.

Of particular interest as restrainers of the oxidative deterioration of fats are the fat-soluble derivatives of ascorbic acid, namely its esters with aliphatic carboxylic acids such as palmitic, stearic, myristic, and lauric acids, the general formula for which can be represented as follows:



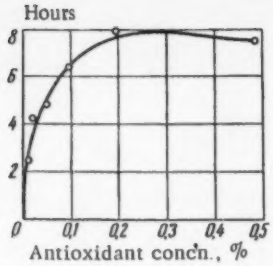


Fig. 2. Relation of the ascorbyl palmitate concentration and the time τ required for the attainment of a peroxide value of 0.1 for lard.

in which R is the hydrocarbon group of the fatty acid. Various such derivatives were synthesized in the U.S. by Wells and Swern [6-8], Swern, Stirton, Turer, and Wells [9], and Wells and Riemenschneider [10]. It was shown that these esters raise the stability to oxidation of lard, cotton oil, and other fats, particularly in presence of tocopherols and phospholipides [11].

However, they do not retard the oxidative processes when the natural tocopherols and phospholipides cannot survive in fats and oils under the conditions of technological treatment. Nevertheless, this indicates that fat-soluble ascorbic esters have synergistic properties, on account of which they are recommended, and in some countries have found practical application, as synergistic antioxidants for fats, oils, and similar substances.

It is convenient to follow the oxidative changes occurring in a fat by studying the accumulation in the system of the primary oxidation products, peroxides. To characterize the rate of the process we may take the time required to attain a definite peroxide value, e.g. 0.1. The choice of this value is associated first with the fact that rendered animal fat oxidized to this extent ceases to be suitable for use as food and second with the fact that at about this value there is a sudden development of oxidative processes in the system, i.e. the oxidation enters into a new stage, the stage of rapid deep-seated oxidation. The effectiveness of a given substance as an antioxidant can be characterized as the ratio of the times for the attainment of 0.1 in systems containing and not containing the antioxidant, τ / τ_0.

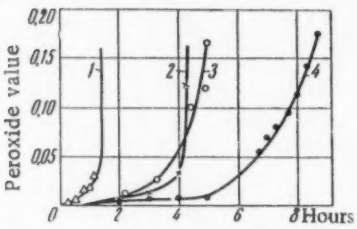


Fig. 3. Kinetic curves for the oxidation of lard:
1) without addition (control); 2) addition of 0.02% of ascorbyl palmitate; 3) addition of 0.01% of tert-butylmethoxyphenol; 4) addition of 0.02% of ascorbyl palmitate + 0.01% of tert-butylmethoxyphenol. Temperature of oxidation 121°.

As in practice we meet the oxidation of fats at room temperature and at the temperatures of refrigerators, it is important to know the effectiveness of antioxidants under these conditions. However, as we showed in our work [20] on the effect of tert-butylmethoxyphenol on the oxidation of lard, this quantity is independent of temperature, so that antioxidants can be tested by an accelerated method at 80-120°, at which temperature a peroxide value of 0.1 is attained in a few hours.

In the present investigatigation, with the aid of an accelerated kinetic method of oxidation at elevated temperature [21], we studied the antioxidation properties of ascorbyl palmitate and mixtures of ascorbyl palmitate with tert-butylmethoxyphenol in the oxidation of lard. We also determined the possibility of replacing palmitic acid by a mixture of normal acids obtained by the oxidation of paraffin (C_{14}–C_{16} fraction) in the preparation of the antioxidant.

EXPERIMENTAL

In the preparation of ascorbyl palmitate, a mixture of 8.8 g of ascorbic acid, 9.9 g of palmitic acid, and 100 ml of 95% sulfuric acid was prepared in a 250-ml conical flask, stirred for a time, and then set aside for 16-18 hours at room temperature. The mixture was poured onto crushed ice (500 g) with vigorous stirring, which was continued until the upper layer froze. The mixture was than extracted with ether, and the ether extract was washed with water until neutral and dried over calcined sodium sulfate. Ether was distilled off, and the residue was ground to a powder and washed by decantation with four 75-ml portions of petroleum ether (b.p. 35-60°) to remove residual palmitic acid. The yield of product of m.p. ranging from 88-89° to 91-92° varied from synthesis to synthesis in the range 8-22% of theoretical.

In the same way we prepared esters of ascorbic acid with the C_{14}–C_{16} fraction of synthetic fatty acids obtained by the oxidation of paraffin. tert-Butylmethoxyphenol was synthesized by the alkylation of p-methoxyphenol with isobutene in a medium of sulfuric or phosphoric acid.

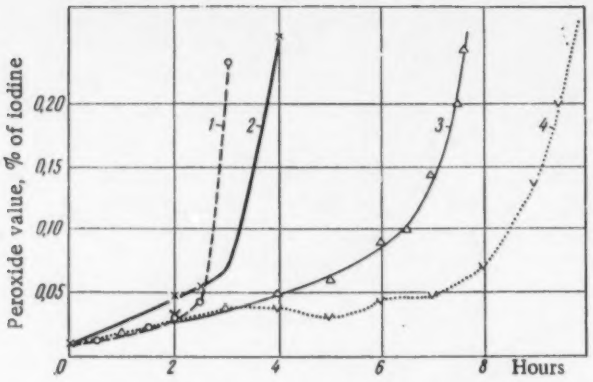


Fig. 4. Kinetic curves for the oxidation of rendered beef suet: 1) without addition (control); 2) addition of 0.02% of ascorbyl palmitate; 3) addition of 0.015% of tert-butylmethoxyphenol; 4) addition of a mixture of 0.02% of ascorbyl palmitate and 0.015% of tert-butylmethoxyphenol. Temperature of oxidation 120°

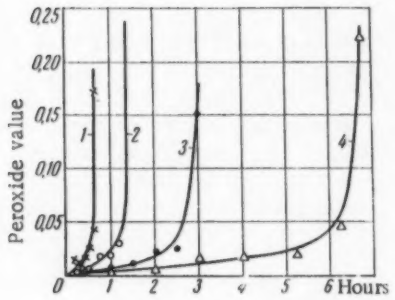


Fig. 5. Kinetic curves for the oxidation of lard at various temperatures: 1) 131°; 2) 121°; 3) 111°; 4) 100°.

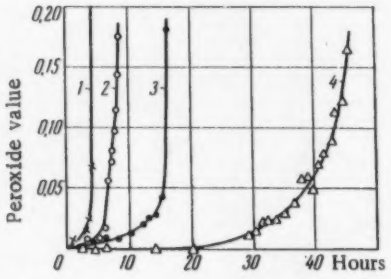


Fig. 6. Kinetic curves for the oxidation of lard in presence of 0.01% of tert-butyl methoxylphenol and 0.02% of ascorbyl palmitate at various temperatures: 1) 131°; 2) 121°; 3) 111°; 4) 100°.

The oxidation was carried out in an oxidation cell, which was placed in a thermostat. Air passing from a porous glass filter sealed into the bottom of the cell bubbled through the melted fat. From time to time test samples of fat were taken from the cell, and their peroxide values were determined by the usual iodometric method. Oxidation was continued until peroxide vales of several tenths were attained; the peroxide values were expressed as percent iodine.

Fig. 1 shows kinetic curves for the oxidation of lard without antioxidant and with various preparations of ascorbic esters. It will be seen that the activities of the preparation differ, and the sample obtained by use of the mixture of synthetic fatty acids is not inferior in its properties to the best of the samples of ascorbyl palmitate.

Fig. 2 shows the effect of the ascorbyl palmitate concentration on the stability of lard to oxidation. It follows from Fig. 2 that the time τ for the attainment of a peroxide value of 0.1 increases with increase in the concentration of ascorbyl palmitate only until a certain limit is reached, and further increase in concentration is then ineffective.

In Fig. 3 we compare the effects of 0.01% of tert-butylmethoxyphenol, 0.02% of ascorbyl palmitate, and a mixture of 0.01% tert-butylmethoxyphenol and 0.02% of ascorbyl palmitate on a given sample of lard. It will be

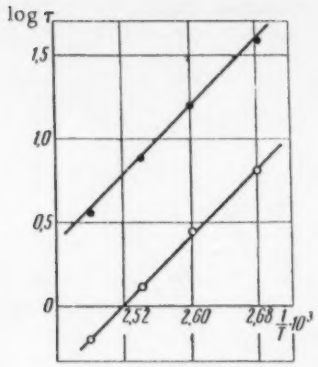


Fig. 7. Relation of the time τ for the attainment of a given peroxide value to the temperature for lard in absence of inhibitor and in presence of 0.01% of tert-butylmethoxyphenol + 0.02% ascorbyl palmitate.

seen that ascorbyl palmitate greatly retards the oxidation of lard; in this case its effectiveness is close to that of tert-butylmethoxyphenol. The mixture of the two antioxidants is particularly effective.

When present separately in these concentrations in the given sample of lard, ascorbyl palmitate and tert-butylmethoxyphenol increase the time required for the attainment of a peroxide value of 0.1 by 2.8 and 3.0 hours respectively, and when present together the increase is 6.7 hours. Hence, ascorbyl palmitate shows some synergism with respect to tert-butylmethoxyphenol.

A mixture of the ascorbic ester and tert-butylmethoxylphenol shows some synergism also in those samples of fat whose oxidation is only weakly inhibited by ascorbyl palmitate. Fig. 4 shows the kinetics of the oxidation of a sample of beef suet in presence of 0.015% of tert-butylmethoxyphenol, 0.02% of ascorbyl palmitate, and a mixture of 0.015% of terty-butylmethoxyphenol and 0.02% of ascorbyl palmitate. Of various samples of beef suet tried we specially selected a sample whose oxidation was only weakly inhibited by ascorbyl palmitate at a concentration of 0.02%. The addition of 0.02% of ascorbyl palmitate increased the time required for the attainment of a peroxide value of 0.1 by only 0.6 hour (by a factor of 1.2), and the addition of terty-butylmethoxylphenol under the same conditions increased the time of oxidation by 4.8 hours (2.5 times as long). Addition of a mixture of the same amounts of the two substance was more effective than their separate additions, the time of oxidation being increased by 6.8 hours, as compared with the control sample.

TABLE

Time τ for the Attainment of a Peroxide Value of 0.1 in the Oxidation of Lard

Temperature (°C)	Time (hours)		
	without antioxidant (τ_0)	with antioxidant (τ_0)	$\frac{\tau_a}{\tau_0}$
100	6.5	43.2	6.6
111	2.85	16.0	5.6
121	1.35	7.8	5.8
131	0.63	4.0	6.3

In this system, therefore, it appears that ascorbyl palmitate again shows some synergism with respect to tert-butylmethoxyphenol.

In order to determine whether the effectiveness of the antioxidant depends on temperature, we determined kinetic curves for the oxidation of lard at four temperatures in presence of a mixture of 0.01% of tert-butylmethoxyphenol and 0.02% of ascorbyl palmitate and in absence of antioxidant (Fig. 5 and 6). The table gives the time τ for the attainment of a peroxide value of 0.1 in presence and in absence of antioxidant.

According to the experimental data in the table, the ratio of these times is almost independent of the temperature. This is confirmed by the determination of the activation energy for the oxidation. In the calculation of the activation energy it was assumed that the reaction rate was inversely proportional to τ; since the rate of

a chemical reaction rises with temperature in accordance with the Arrhenius equation

$$w = Ae^{-\frac{E}{RT}},$$

τ should fall with rise of temperature in accordance with the law

$$\tau = Be^{\frac{E}{RT}}$$

and a linear relation between $\log\tau$ and $1/T$ should be observed. It will be seen from Fig. 7 that this relation is closely obeyed and that the straight lines obtained for oxidation in presence of antioxidant and for oxidation in absence of antioxidant are almost parallel. The activation energies are 23.6 kcal/mole in presence of the mixture of antioxidants and 23.1 kcal/mole in absence of antioxidants, i. e. almost identical.

SUMMARY

1. In admixture with tert-butylmethoxyphenol, ascorbyl palmitate effectively retards air-oxidation processes in rendered animal fats.

2. Replacement of palmitic acid by a mixture of synthetic fatty acids (C_{14}–C_{16} fraction) in the preparation of ascorbic esters does not affect their antioxidant properties deleteriously.

3. The effectiveness of a mixture of 0.01% of tert-butylmethoxyphenol and 0.02% ascorbyl palmitate as an antioxidant for rendered animal fats does not depend on the temperature of oxidation.

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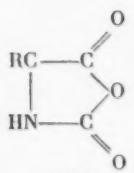
KINETICS AND CHEMISTRY OF THE POLYCONDENSATION OF α-AMINO ESTERS

COMMUNICATION 7. KINETICS OF THE CHANGE IN THE COMPOSITION OF THE PRODUCTS OF THE POLYCONDENSATION OF GLYCINE ETHYL ESTER IN PRESENCE OF N-CARBOXYGLYCINE ANHYDRIDE

K. T. Poroshin, Iu. I. Khurgin, and N. I. Prokhorova

Synthetic polypeptides (poly-α-amino-acids) are generally prepared from derivatives of α-amino acids under the action of specific initiators. In our preceding communication we proposed a mechanism for the polycondensation of α-amino esters for the case of initiation by carbon dioxide [1]. It was shown that in the polycondensation the symmetrical carbamate $R'OOC \cdot CHR \cdot NH_3^+ \cdot {}^-OOC \cdot NH \cdot CHR \cdot COOR'$ (I) reacts with amino esters or peptides with formation of simple unsymmetrical carbamates $R'OOC \cdot CHR \cdot NH_3^+ \cdot {}^-OOC(NH \cdot CHRCO)_nOR'$ (II). In this the active intermediate compound is the carbamate (I), which is formed quantitatively in the reaction between carbon dioxide and α-amino esters [2, 3]. In the decomposition of the intermediate unsymmetrical carbamates (II) peptides are formed which contain one amino-acid residue more than the original peptide ester (or amino ester) reacting with the simple carbamate (I). Hence, in the polycondensation of α-amino esters a leading part is played by derivatives of α-(carboxyamino) acids (the carbamates (I) and (II)).

For the preparation of poly-α-amino-acids extensive use is made of α-(carboxyamino) acid anhydrides (III):



(III)

Among other initiators used in the polycondensation of α-(carboxyamino) acid anhydrides are various hydroxy and amino compounds. An investigation of the mechanism of initiation by various amines was carried out by Ballard and Bamford [4, 5]. Blaut, Doty, and co-workers [6, 7] established the effects of the relative concentration of the amine, of its nature, and of reaction conditions such as temperature, nature of solvent, and concentrations of reactants on the composition and spatial configuration of the reaction products. The kinetics of the polycondensation were investigated by Ballard and Bamford [4], Waley and Watson [8], Breitenbach and Allinger [9], and others. In an investigation of the kinetics of the polycondensation of the benzyl ester of N-carboxyglutamic N,1-cyclic anhydride at low relative concentrations of initiator, Doty and Lundberg [10] found that, in agreement with the data of the other workers, the consumption of the anhydride (III) corresponded to a first-order law. However, when the mean degree of polymerization attains 6-8 the rate constant increases suddenly by a factor varying according to experimental conditions from 4 to 6. We must here point out that analysis of Doty and Lundberg's data [10] shows that at the very beginning of the reaction a very rapid stage should be observed, for in the extrapolation of the first (slow) linear section of the kinetic curve (on a semilogarithmic scale) the axis of abscissae is crossed at a point below that corresponding to the initial concentration of the anhydride.

Apart from other amines, α-amino acids or peptides with a substituted carboxy group (amides [4] and esters

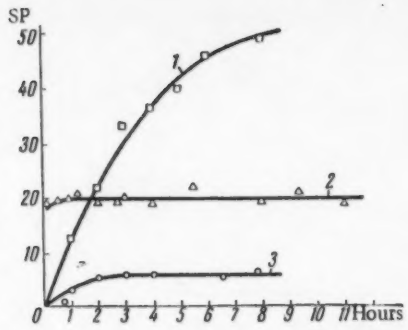


Fig. 1. Yield (%) of copolycondensation products:
1) A/E = 0.08 (in the mass); 2) A/E = 0.08 (in 5% solution).

[11] of these compounds) are sometimes used as initiators. Also, the interaction of α-amino esters with α-(carboxyamino) acid anhydrides may be applied inthe synthesis of di- and tri-peptides of given structure [12]. However, because of the low yield and the occurrence of side reactions (polycondensation of the ester and the formation of piperazinediones) this method of synthesis has not found wide application. By replacement of the anhydrine (III) by the corresponding dithio analog (2-thio-2,5-thiazolidinedione), Cook and Levy [13] carried out this reaction very successfully. In this synthesis of peptides, unsymmetrical carbamates (II) or the corresponding dithiocarbamates are formed as intermediaries. Carbamate compounds of type (II) have been isolated and characterized by several authors [2, 3, 12, 14]. The possibility of forming carbamates (II) in the polymerization of α-(carboxyamino) acid anhydrides is discussed by Ballard and Bamford [4]. Hence, identical active intermediate carbamates (II) are formed both in the polymerization of α-(carboxyamino) acid anhydrides in presence of amine initiators and in the polycondensation of α-amino esters in presence of carbon dioxide

We have previously showed [15] that it is possible to copolycondense N-carboxyglycine anhydride with glycine ethyl ester. When the relative amounts of N-carboxyglycine anhydride are small, it acts as initiator for the polycondensation of glycine ethyl ester. At that time we proposed a scheme for mutual initiation in the copolycondensation.

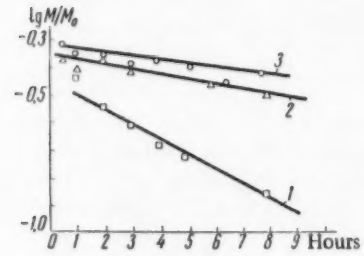
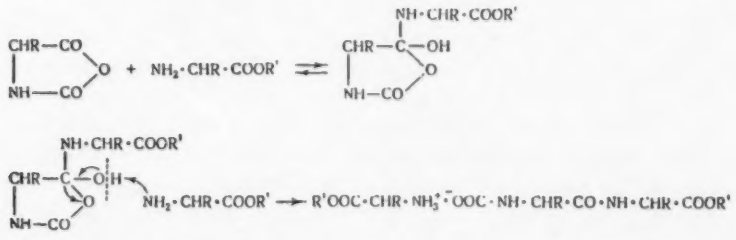


Fig. 2. Kinetics of the consumption of glycine ethyl ester in the course of copolycondensation:
1) A/E=0.08 (in the mass); 2) A/E = 0.5 (in 5% solution); 3) A/E = 0.08 (in 5% solution).

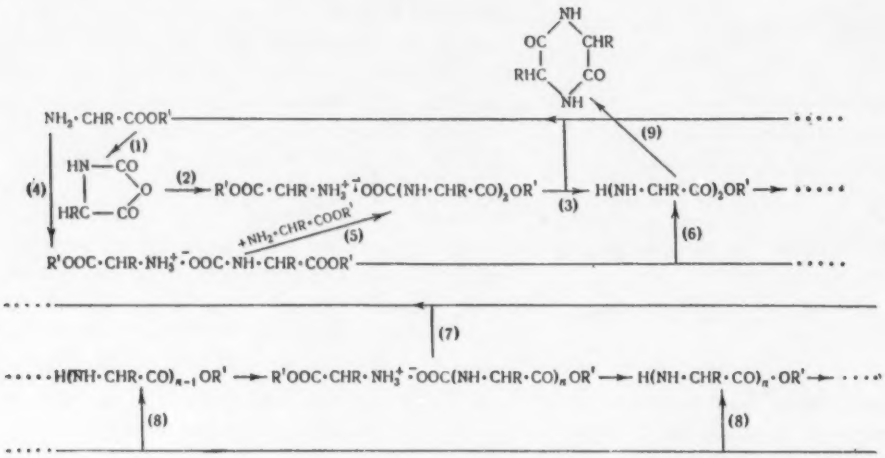
According to this scheme, as a result of the reaction of the amino ester with the carboxyamino acid anhydride there is initial rapid formation of the unsymmetrical carbamate (II) (n = 2), which decomposes with formation of CO_2, the dipeptide ester, and the amino ester. Further reaction proceeds by the previously proposed mechanism [1] for the polycondensation of α-amino esters in presence of carbon dioxide. The initiation of the polymerization of α-(carboxyamino) acid anhydrides by the alcohol liberated does not play any substantial part, because before an appreciable amount of alcohol accumulates the whole of the anhydride is used up. Hence, at the start of the reaction some of the amino ester must rapidly enter into combination with formation of the primary intermediate carbamate. Subsequently, the glycine ethyl ester is slowly used up in the lengthening of the peptide chains already being formed and in the formation of new ones by the mechanism of the polycondensation of α-amino esters [1], which is indicated by the presence in the polycondensation products of a considerable amount of piperazinedione, a typical product of the polycondensation of α-amino esters. In the polymerization of α-(carboxyamino) acid anhydrides, piperazinedione is formed in small amounts [16, 17] (to increase the yield of piperazinedione specially severe conditions are necessary [18]).

In the first stage of the reaction the α-(carboxyamino) acid anhydride reacts in the following manner with the α-amino ester [4, 14], which reacts at this stage as a primary amine:



In the second, slower stage, the polycondensation of α-amino esters in presence of the α-(carboxyamino) acid anhydride proceeds by the mechanism for the polycondensation of α-amino esters in presence of carbon dioxide [1] with formation of intermediate carbamates.

It may be considered, therefore, that the mechanism of the copolycondensation proceeds according to the following scheme, in which the sequence of reactions (1)-(2) characterizes the first stage of the reaction and the sequence (4)-(9) the second.



The present communication gives the results of an investigation into the kinetics of the copolycondensation of an α-amino ester and an α-(carboxyamino) acid anhydride for the case of the glycine derivatives and into the effect of the relative concentration of the anhydride (A/E) on the composition of the reaction products.

EXPERIMENTAL

The copolycondensation of glycine ethyl ester was initiated by an addition of N-carboxyglycine anhydride. As the polycondensation proceeds vigorously, the reaction mixture solidifies fairly rapidly and reaction then proceeds in a heterogeneous medium. It was therefore found to be more convenient to investigate this reaction in solution. As solvent we selected dioxane, in which the reactants (N-carboxyglycine anhydride and the glycine ester) and a considerable part of the reaction products are readily soluble. Moreover, because of the high freezing point of dioxane (9°) the reaction can be stopped at the required moment; also, in the isolation of the solid reaction products the dioxane can be rapidly and completely removed under reduced pressure at a fairly low temperature with consequent avoidance of further polycondensation.

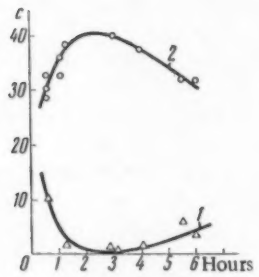


Fig. 3. Content (%) in solid phase of copolycondensation products (A/E = 0.5):
1) dipeptide ester;
2) tripeptide ester.

Most of the experiments were carried out with a 5% solution of the reactants in dioxane, because at this strength the anhydride is still readily soluble at room temperature and the relative smallness of the amount of solvent makes it possible to isolate the reaction products rapidly. By variation of the content of reactants in the range 0.5-10% it was shown that the amount of solvent has no substantial effect on the course of the reaction.

An exact weight of anhydride was dissolved in a definite amount of dry dioxane, and the necessary amount of glycine ethyl ester was added to the solution. The reaction was carried out in tightly stoppered flasks at the same temperature (40°) as that used in the study of the polycondensation of α-amino esters in presence of carbon dioxide. Change in temperature from 20° to 60° has no appreciable effect on the qualitative composition of the reaction products. At the end of the reaction solvent was distilled off under reduced pressure (10 mm) at a bath temperature of 30°. The dry residue was ground with dry ether, when, as shown previously [12], glycine ethyl ester passes

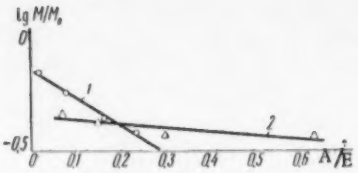


Fig. 4. Effect of A/E on the rate of reaction of monomer:
1) in the mass; 2) in solution.

completely into the ether, whereas the remaining substances remain in the precipitate. The precipitate (solid phase, SP) was weighed; the yield is shown in Fig. 1. The completeness and selectivity of the extraction was verified chromatographically. The amount of unchanged glycine ethyl ester was determined by the previously described method [19].

The qualitative composition of the polycondensation products was studied chromatographically, and the contents of the tetra- and tri-peptide fractions and of piperazinedione were determined by the method of differential titration [20]. The mean degree of polycondensation was determined from Van Slyke amine nitrogen estimations. The amount of unchanged N-carboxyglycine anhydride was generally determined by titration with sodium methoxide [21]. However, we found that, in addition to carboxyamino acid anhydrides, sodium methoxide titrates also the intermediate products of the polycondensation, i.e. the symmetrical and unsymmetrical carbamates. To verify this we synthesized the symmetrical carbamates of the ethyl esters of glycine [3] and glycylglycine [2]. It was found that these carbamates are quantitiatively titrated by sodium methoxide in an anhydrous medium. The results of the titration with sodium methoxide, therefore, correspond to the over-all content of carbamates and α-(carboxyamino) acid anhydride in the condensation products. N-carboxyglycine anhydride reacts extremely rapidly with glycine ester, and it is therefore probable that the results of this method correspond to only carbamates in the polycondensation products. Chromatographic analysis showed that the compositions of the polycondensation products of glycine ethyl ester obtained by initiation with carbon dioxide and with N-carboxyglycine were identical [15]. In a chromatographic investigation of the products of polycondensation in presence of N-carboxyglycine anhydride, it was found, previously, that, in distinction to the case of polycondensation in presence of carbon dioxide, an appreciable amount of the dipeptide ester was formed. As the mechanisms of polycondensation have several common features in the two cases, the reaction was first of all studied under conditions close to those used for polycondensation in presence of carbon dioxide [19]. The main characteristic of the reaction conditions was the ratio of the initial molar concentrations of N-carboxyglycine anhydride and glycine ethyl ester (A/E: anhydride/ester).

The copolycondensation was first studied at A/E=0.08. The main indexes of the extent of reaction were the amount of glycine ethyl ester that reacted and the concentration of terminal amino groups. The results of measurements of the amount of unchanged glycine ethyl ester (monomer) after various periods of reaction are shown in Fig. 2. The results show that the reaction can be broken down into two stages. The first is a rapid one and is complete in the course of the first 5-10 minutes, during which about 30% of the original monomer reacts at a fairly high rate. In the second stage of the reaction the monomer is consumed more slowly, and at this stage the consumption of monomer confirms to the kinetics of a first-order reaction. The rate constant for the reaction depends on the concentrations of the reactants in the dioxane. For solutions in which the concentration of reactants is 1-5% the rate constant is of the order of 10^{-7} second $^{-1}$. The rate constant for reaction carried out with addition of solid N-carboxyglycine anhydride in glycine ethyl ester (reaction in the mass) is $3.3 \cdot 10^{-5}$ second^{-1}.

In the polycondensation products after removal of monomers (anhydride and glycine ethyl ester) the content of amine nitrogen was 0.7%, as compared with the initial value of 4.8%. If we take account of the fact that the polycondensation products contained about 10% of piperazinedione, then the mean degree of polymerization was 3.8-5.2 at the end of the reaction, which is the same as that of the polycondensation products obtained from glycine ethyl ester in presence of CO_2 [19]. Actually, chromatographic analysis showed that, though there were some relatively long peptides among the copolycondensation products, the bulk consisted of lower peptides (di- and tri-peptides). In the study of the copolycondensation products we used not only the differential-titration method [20], but also a specially developed method of estimating dipeptide based on the differences in the absorption spectra of the copper biuret complexes of the peptides. We have previously shown that free peptides are absent among the copolycondensation products, only peptide esters being present. On this basis we calculated the concentrations by weight of di- and tri-peptide (Fig. 3).

In a study of polycondensation at A/E=0.5 it was found that the piperazinedione concentration remains unchanged at about 11% in the solid phase over the period from 0.5 to 12 hours. The contents of the tripeptide and "tetrapeptide", fractions also remain constant at about 30 and 40%, respectively, of the solid phase. The consumption

of monomer can be explained by the relatively slow increase in the length of peptides making up the "tetrapeptide" fraction. Qualitative investigation by paper chromatography showed some increase in the contents of penta- and hexa-peptides in the polycondensation products. Thus, at A/E = 0.5 in 5% solution, reaction was essentially complete immediately after the mixing of the solutions of glycine ethyl ester and N-carboxyglycine anhydride, which was accompanied by the formation of a fairly compact precipitate. At the start about 50% of the original amount of glycine ethyl ester enters into the reaction (Fig. 1, Curve 3). At A/E = 0.08 two stages of reaction were again observed. The rapid stage was complete at the end of the first hour of reaction. In this stage the consumption of monomer followed first-order kinetics with a rate constant of $1.64 \cdot 10^{-4}$ $second^{-1}$. The monomer was used up in the formation of tripeptides and the "tetrapeptide fraction", whereas the piperazinedione content of the solid phase fell from 15% to 13%; in the later stages it continued to fall to 11%. It is probable that the piperazinedione is formed in the very earliest stages of the reaction, whereas later, when the other reaction products are accumulating more rapidly, the piperazinedione content of the solid phase falls.

Parallel experiments were carried out without solvent (in the mass). All the processes were considerably more rapid than in solution, though they did not differ qualitatively.

Comparison of the results with those on the polycondensation of glycine ethyl ester in presence of carbon dioxide [19] shows that the regularities to be observed in the courses of the two processes are in the main identical. However, the intermediate products formed in the first stage of the polycondensation are different: addition of CO_2 results in the formation of the symmetrical carbamate $R'OOC \cdot CHR \cdot NH_3^+ \cdot {}^-OOC \cdot NH \cdot CHR \cdot COOR'$; and initiation by a carboxylamino acid anhydride results in the formation of the unsymmetrical carbamate $R'OOC \cdot CHR \cdot NH_3^+ \cdot {}^-OOC \cdot NH \cdot CHR \cdot CO \cdot NH \cdot CHR \cdot COOR'$. This probably explains the observed difference in the rates of the processes and the distribution of the reaction products at the various stages.

We studied also the effect of additions of N-carboxyglycine anhydride in the range of A/E from 0.07 to 0 63 in a 5% solution of the monomers in dioxane and in the range of A/E from p.04 to 0.23 in the mass. All experiments were at 40° for four hours. The results of measurements of the amounts of unchanged monomers are given in Table 4, from which it can be seen that the rate of polycondensation increases with increase in A/E. With increase of A/E to 0.08 the yield of solid phase attains a constant value: 40% for reaction in the mass, and 20% for reaction in solution.

In polycondensation in solution a characteristic reduction in the content of dipeptide with simultaneous increase in the content of tripeptide was observed. With increase in A/E the content of the "tetrapeptide" fraction does not change. Values obtained for the average degree of polymerization of mass-polycondensation products (taking the piperazinedione content of the solid phase into account) were 5.25 and 4.7. Both chromatographic and quantitative studies of the composition of the copolycondensation products showed their closeness to the compositions of polycondensation products obtained in presence of carbon dioxide.

Hence, the reactions of the carboxyamino acid and of carbon dioxide with the α-amino ester pass through identical stages, with the result that the products of these reactions have the same qualitative compositions.

SUMMARY

1. A study was made of the compositions of the products of the mass and solution copolycondensation of glycine ethyl ester with N-carboxyglycine anhydride.

2. A study was made of the kinetics of the change in composition of the polycondensation products of glycine ethyl ester. The effects of the relative concentration of N-carboxyglycine anhydride, the temperature, and the amount of solvent were established.

3. It was found that reaction proceeds in two stages, the occurrence of which may be explained by the mutual-initiation mechanism.

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SYNTHESIS OF ORGANIC COMPOUNDS OF QUINQUEVALENT ANTIMONY BY THE ARYLATION OF THE ORGANOANTIMONY COMPOUNDS $ArSbX_2$ AND Ar_2SbX WITH DIAZO COMPOUNDS

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As we have shown previously [1], by the use of an excess of the double salt formed by a diazonium salt with antimony chloride, it is possible to direct the course of the reaction for the preparation of organoantimony compounds developed by one of us and Kocheshkov [2] so that only one product, diphenylantimony trichloride, is formed. We consider that the formation of this substance proceeds via the arylation of aryldichlorostibine by May's salt as follows:

$$C_6H_5N_2Cl \cdot SbCl_3 + Zn \rightarrow C_6H_5SbCl_2 + N_2 + ZnCl_2,$$
$$C_6H_5SbCl_2 + C_6H_5N_2Cl \cdot SbCl_3 \rightarrow (C_6H_5)_2SbCl_3 + N_2 + SbCl_3.$$

To verify this suggestion we studied the reaction of dichlorophenylstibine with May's salt in acetone in the cold. It was found that dichlorophenylstibine was indeed arylated with formation of diphenylantimony trichloride [3].

As the very small amount of data reported in the literature on the arylation of organoantimony compounds with diazonium compounds [4-7] is of a tentative character, in the continuation of our work on this reaction we have made a detailed investigation of the possibility of the arylation of compounds of the type $ArSbX_2$ and Ar_2SbX with the aid of diazo compounds and various double diazonium salts. As a result we have found conditions which make it possible to bring about arylation very readily in high yields. The reactions that we have studied can be summarized by the following general schemes:*

$$ArSbX_2 + Ar'N_2Y \rightarrow \begin{matrix} Ar & X \\ \diagdown & \diagup \\ Sb & -X \\ \diagup & \diagdown \\ Ar' & Y \end{matrix} + N_2$$

$$ArSbX_2 + Ar'N_2XMeX_n \rightarrow \begin{matrix} Ar & X \\ \diagdown & \diagup \\ Sb & -X \\ \diagup & \diagdown \\ Ar' & X \end{matrix} + N_2 + MeX_n$$

$$Ar_2SbX + Ar'N_2Y \rightarrow \begin{matrix} Ar & X \\ \diagdown & \diagup \\ Ar-Sb & \\ \diagup & \diagdown \\ Ar' & Y \end{matrix} + N_2$$

$$Ar_2SbX + Ar'N_2X \cdot MeX_n \rightarrow \begin{matrix} Ar & X \\ \diagdown & \diagup \\ Ar-Sb & \\ \diagup & \diagdown \\ Ar' & X \end{matrix} + N_2 + MeX_n .$$

* In these equations X and Y represent Cl, I or CH_3COO, and Me represents Sb or Zn.

TABLE

No.	Compound arylated	Arylating agent	Reaction product (yield, %)	Form in which reaction product identified (m.p., °C)
1	$p\text{-}CH_3C_6H_4SbCl_2$	$C_6H_5N_2OCOCH_3$	$C_6H_5(p\text{-}C_7H_7)Sb(=O)OH$ * (92)	$C_6H_5(p\text{-}C_7H_7)SbCl_2$ (150—151,5)
2	$p\text{-}CH_3C_6H_4SbCl_2$	$p\text{-}CH_3C_6H_4N_2OCOCH_3$	$(CH_3C_6H_4)_2Sb(=O)OH$ (20)	$(CH_3C_6H_4)_2SbCl_3$ (155)
3	$p\text{-}CH_3C_6H_4SbCl_2$	$C_6H_5N_2Cl\cdot SbCl_3$	$C_6H_5(CH_3C_6H_4)Sb(=O)OH$ (45)	$C_6H_5(CH_3C_6H_4)SbCl_2\cdot C_6H_5N_2Cl$ (63—64 decomp.)
4	$p\text{-}CH_3C_6H_4SbCl_2$	$p\text{-}ClC_6H_4N_2Cl\cdot SbCl_3$	$(CH_3C_6H_4)(ClC_6H_4)Sb(=O)OH$ (45)	$(CH_3C_6H_4)(ClC_6H_4)SbCl_2$ $p\text{-}ClC_6H_4N_2Cl$ (120—121 decomp.)
5	$p\text{-}CH_3C_6H_4SbCl_2$	$p\text{-}O_2NC_6H_4N_2Cl\cdot SbCl_3$	$(CH_3C_6H_4)(O_2NC_6H_4)Sb(=O)OH$ (87)	$(CH_3C_6H_4)(O_2NC_6H_4)SbCl_2\cdot C_6H_5N_2Cl$ (74—76 decomp.)
6	$p\text{-}CH_3C_6H_4SbCl_2$	$(p\text{-}CH_3OC_6H_4N_2Cl)_2ZnCl_2$	$(CH_3C_6H_4)(CH_3OC_6H_4)Sb(=O)OH$ (32)	$(CH_3C_6H_4)(CH_3OC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (98 decomp.)
7	$C_6H_5SbCl_2$	$p\text{-}ClC_6H_4N_2Cl\cdot SbCl_3$	$C_6H_5(ClC_6H_4)Sb(=O)OH$ (60)	$C_6H_5(ClC_6H_4)SbCl_2\cdot p\text{-}ClC_6H_4N_2Cl$ (109 decomp.)
8	$p\text{-}CH_3C_6H_4SbI_2$	$p\text{-}CH_3OC_6H_4N_2Cl\cdot SbCl_3$	$(CH_3C_6H_4)(CH_3OC_6H_4)Sb(=O)OH$ (66)	$(CH_3C_6H_4)(CH_3OC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (99—100 decomp.)
9	$p\text{-}CH_3C_6H_4SbI_2$	$p\text{-}CH_3C_6H_4N_2Cl\cdot SbCl_3$	$(CH_3C_6H_4)_2Sb(=O)OH$ (84)	$(CH_3C_6H_4)_2SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (103—104 decomp.)
10	$p\text{-}ClC_6H_4SbI_2$	$C_6H_5N_2Cl\cdot SbCl_3$	$C_6H_5(ClC_6H_4)Sb(=O)OH$ (95)	$C_6H_5(ClC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (94—96 decomp.)
11	$p\text{-}ClC_6H_4SbI_2$	$p\text{-}CH_3C_6H_4N_2Cl\cdot SbCl_3$	$(CH_3C_6H_4)(ClC_6H_4)Sb(=O)OH$ (85)	$(CH_3C_6H_4)(ClC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (102 decomp.)
12	$p\text{-}ClC_6H_4SbI_2$	$p\text{-}CH_3OC_6H_4N_2Cl\cdot SbCl_3$	$(ClC_6H_4)(CH_3OC_6H_4)Sb(=O)OH$ (69)	$(ClC_6H_4)(CH_3OC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (122—124 decomp.)
13	$p\text{-}ClC_6H_4SbI_2$	$p\text{-}ClC_6H_4N_2Cl\cdot SbCl_3$	$(ClC_6H_4)_2Sb(=O)OH$ (86)	$(ClC_6H_4)_2SbCl_3\cdot p\text{-}CH_3C_6H_4N_2Cl$ (101 decomp.)
14	$p\text{-}ClC_6H_4SbI_2$	$p\text{-}O_2NC_6H_4N_2Cl\cdot SbCl_3$	$(ClC_6H_4)(O_2NC_6H_4)Sb(=O)OH$	$(ClC_6H_4)(O_2NC_6H_4)SbCl_2\cdot p\text{-}CH_3C_6H_4N_2Cl$ (103—104 (decomp.)
15	$(C_6H_5)_3SbOCOCH_3$	$C_6H_5N_2OCOCH_3$	$(C_6H_5)_2Sb(OCOCH_3)_3$ (26)	$(C_6H_5)_3SbCl_2$ (142—143)
16	$(p\text{-}CH_3C_6H_4)_3SbOCOCH_3$	$p\text{-}CH_3C_6H_4N_2OCOCH_3$	$(CH_3C_6H_4)_2Sb(OH)(OCOCH_3)$ (59)	$(C_7H_7)_2Sb(OH)(OCOCH_3)$ (166—167)
17	$(o\text{-}ClC_6H_4)_3SbCl$	$o\text{-}ClC_6H_4N_2Cl\cdot SbCl_3$	$(o\text{-}ClC_6H_4)_2SbCl_3$ (73; m.p. 204—206°)	—
18	$(o\text{-}ClC_6H_4)_3SbCl$	$p\text{-}O_2NC_6H_4N_2Cl\cdot SbCl_3$	$ClC_6H_4(ClC_6H_4)(O_2NC_6H_4)SbCl_2$ (45; m.p. 202°)	—
19	$(o\text{-}C_2H_5OC_6H_4)_3SbCl$	$(o\text{-}ClC_6H_4N_2Cl)_2ZnCl_2$	$(C_2H_5OC_6H_4)_2(ClC_6H_4)SbCl_2$ (74; m.p. 189—190°)	—
20	$(o\text{-}C_2H_5OC_6H_4)_3SbCl$	$p\text{-}O_2NC_6H_4N_2Cl\cdot SbCl_3$	$(C_2H_5OC_6H_4)_2(O_2NC_6H_4)SbCl_2$ (82; m.p. 230°)	—

* All the stibinic acids were obtained by hydrolysis of the compounds formed (of the type $ArAr'SbX_3$) with aqueous ammonia.

The use of several different substances as arylating agents (aryldiazoacetates, double diazonium-antimony chlorides, double diazonium-zinc chlorides) was prompted by the fact that each of these substances reacts readily only with a limited range of organoantimony compounds. The least reactive are the double diazonium-zinc chlorides, and the most reactive are the are aryldiazoacetates but by no means are all of these compounds readily available.

In the treatment of $ArSbCl_2$ or Ar_2SbCl with double diazonium salts, the ease, or even possibility, of the arylation reaction depends both on the character of the diazonium salt and also on the character of the organic groups in the organoantimony compound to be arylated. Thus, the reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $C_6H_5N_2Cl \cdot SbCl_3$ goes vigorously in the cold, whereas $p\text{-}CH_3C_6H_4SbCl_2$ does not react with $p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_3$ even at the temperature of boiling acetone. Again, $(o\text{-}ClC_6H_4)_2SbCl$ and $(o\text{-}ClC_6H_4N_2Cl)_2ZnCl_2$, and also $(o\text{-}C_2H_5OC_6H_4)_2SbCl$ and $(o\text{-}C_2H_5OC_6H_4N_2Cl)_2ZnCl_2$, do not react in boiling acetone solutions, but $(o\text{-}C_2H_5OC_6H_4)_2SbCl$ and $(o\text{-}ClC_6H_4N_2Cl)_2ZnCl_2$ react readily in the cold; and so on.

Among the double diazonium-antimony chlorides the best reagents are those in which the aromatic groups contain m-orientators. Double diazonium salts containing powerful o,p-orientators on the other hand, do not arylate at all. Thus, the double salt $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$ arylates compounds of the types $ArSbCl_2$ and Ar_2SbCl irrespective of the character of Ar, whereas the double salt $[p\text{-}(CH_3)_2NC_6H_4N_2Cl]_2SbCl_3$ reacts neither with aryldichlorostibines nor with diarylchlorostibines, even when heat is applied. The character of the aryl group in $ArSbCl_2$ and Ar_2SbCl also affects the readiness with which the arylation goes, but its effect appears to be less marked than that of the aryl group in the double diazonium salt.

It must be pointed out that a general method of synthesis of mixed organoantimony compounds of the type $ArAr'SbX_3$ has been found in the action of double diazonium-antimony chlorides on aryldiiodostibines which are readily prepared from aryl stibates. In almost all cases reaction goes in the cold and results in the formation of the corresponding organoantimony compounds in high yields. The compounds $ArAr'SbX_3$ were isolated in the form of diarylstibinic acids and were identified in the form of the double diazonium salts $ArAr'SbCl_3 \cdot Ar''N_2Cl$ by the method developed by one of us and Markovskaia [8]:

$$ArAr'Sb(=O)(HO) \xrightarrow{\text{alcoholic HCl}} ArAr'SbCl_3,$$

$$ArAr'SbCl_3 + Ar''N_2Cl \cdot FeCl_3 \rightarrow ArAr'SbCl_3 \cdot Ar''N_2Cl + FeCl_3.$$

The results of our study of the arylation of organoantimony compounds of the types $ArSbX_2$ and Ar_2SbX with the aid of aryldiazoacetates and double diazonium salts are given in the table.

The here described preparative method for the synthesis of substances of the types $ArAr'SbX_3$ and $Ar_2Ar'SbX_2$ supplements the methods that we have developed previously [2, 8-11] for the preparation of substances of these classes in very important respects.

EXPERIMENTAL

1. Preparation of Dichloro-p-tolylstibine. p-Stibosotoluene (5 g) was dissolved in glacial acetic acid (10 ml) at room temperature, and the resulting solution was cooled while 15 ml of 5 N HCl was added. With the addition of the first portions of thehydrochloric acid there appeared a precipitate, which gradually dissolved; but later a precipitate was again formed. The product, amounting to 3.5 g (58%), was dichloro-p-tolylstibine, m.p. 91-92° (the literature [12] gives 89-92°).

2. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $C_6H_5N_2OCOCH_3$. To a solution of 7 g (0.025 mole) of dichloro-p-tolylstibine in 50 ml of acetone, 8 g (0.05 mole) of benzenediazoacetate was added. To start the reaction the mixture was heated to the boil in a water bath, and an exothermic reaction then set in and was complete in an hour. Solvent was distilled off, and the residue was washed with 5 N HCl; five volumes of cold alcohol was then added. The alcohol-insoluble precipitate (I), which was a white substance, was filtered off. With good external cooling the alcoholic filtrate was poured into ammonia solution. The precipitated phenyl-p-tolylstibinic acid was filtered off and washed with water, alcohol, and ether; yield 5.6 g (71%).

Found %: C 48.09; 47.92; H 4.05; 3.99; Sb 37.53; 37.72 $C_{13}H_{13}O_2Sb$. Calculated %: C 48.34; H 4.06; Sb 37.68

By crystallization of $C_6H_5(p\text{-}C_7H_7)SbOOH$ from 5 N HCl we obtained phenyl-p-tolylantimony trichloride, m.p. 150-151.5°.

Found %: C 39.35; 39.30; H 3.33; 3.26 $C_{13}H_{12}Cl_3Sb$. Calculated %: C 39.40; H 3.05

The alcohol-insoluble precipitate (I) was probably partially hydrolyzed phenyl-p-tolylantimony trichloride, for it gave $C_6H_5(p\text{-}C_7H_7)SbCl_3$, when heated with 5 N HCl. The total yield was 92% on the phenyl-p-tolylstibinic acid.

3. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $p\text{-}CH_3C_6H_4N_2OCOCH_3$. To the solution of 5 g (0.0176 mole) of dichloro-p-tolylstibine in 40 ml of acetone, 5.5 g (0.031 mole) of p-tolyldiazoacetate was added. The reaction mixture was heated for a short time at the boil, and vigorous evolution of nitrogen set in and reaction proceeded with evolution of much heat. During the reaction precipitation of a double salt occurred; analysis indicated that the salt had the composition $C_7H_7Sb(OCOCH_3)_2 \cdot C_7H_7N_2OCOCH_3$. The double salt was washed thoroughly with acetone-weight 4.1 g; m.p. 122-123° (decomp.).

Solvent was distilled from the filtrate; the residue was washed with 5N HCl and then diluted with five times its volume of alcohol and 5 ml of acetone. From the alcohol-acetone solution we isolated 1.2 g further of the double salt $C_7H_7Sb(OCOCH_3)_2 \cdot C_7H_7N_2OCOCH_3$. The total yield of this substance was 5.3 g (60%); m.p. 122-123° (decomp.).

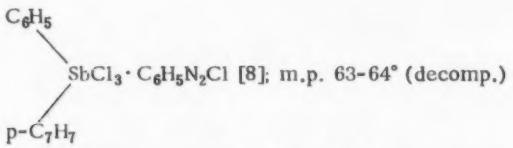
Found %: Sb 23.63; 23.82; N 5.83; 5.99 $C_{20}H_{23}N_2O_6Sb$. Calculated %: Sb 23.92; N 5.50

The alcohol-acetone filtrate was poured into ammonia solution. The precipitated di-p-tolylstibinic acid was filtered off and washed with water, alcohol, and ether; yield 1.2 g (20%).

Crystallization of $(p\text{-}CH_3C_6H_4)_2SbOOH$ from 5 N HCl gave di-p-tolylantimony trichloride, m.p. 155° (the literature [13] gives 155°). There was depression of melting point in admixture with known $(p\text{-}CH_3C_6H_4)_2SbCl_3$.

Found %: C 40.22; 40.32; H 3.65; 3.63 $C_{14}H_{14}Cl_3Sb$; Calculated %: C 40.97; H 3.44

4. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $C_6H_5N_2Cl \cdot SbCl_3$. To a solution of 2 g (0.007 mole) of dichloro-p-tolylstibine in 20 ml of acetone, 4 g (0.01 mole) of $C_6H_5N_2Cl \cdot SbCl_3$ was added. Reaction was very vigorous in the cold. When the evolution of nitrogen ceased, the excess of May's salt was filtered off and the solvent was evaporated. The residual thick mass was washed with 5 N HCl, and 25 ml of alcohol was then added. Some double salt (0.5 g) was isolated from the alcohol, but was not investigated further. On pouring the alcoholic solution, we obtained 1 g of phenyl-p-tolylstibinic acid (45% yield). The acid was identified in the form of the double salt

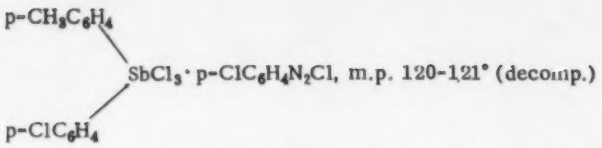


Found %: Sb 22.40; 22.63 $C_{19}H_{17}N_2Cl_4Sb$. Calculated %: Sb 22.65

5. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$. To solution of 3 g (0.011 mole) of dichloro-p-tolylstibine in 25 ml of acetone, 6 g (0.014 mole) of $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$ was added. Reaction was slow in the cold, and to complete it was necessary to apply heat. Treatment similar to that of Experiment 4 gave 3.8 g of a mixture of double diazonium salts, from which, by dissolution in acetone and precipitation with ether, we isolated the double salt $(p\text{-}C_7H_7)(p\text{-}ClC_6H_4)SbCl_3 \cdot p\text{-}ClC_6H_4N_2Cl$, m.p. 117-118° (decomp.).

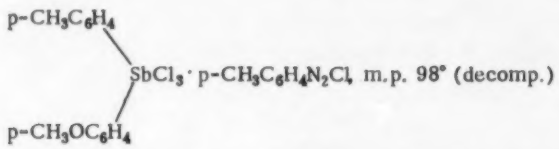
Found %: Sb 20.49 $C_{19}H_{15}N_2Cl_6Sb$. Calculated %: Sb 20.10

By pouring the alcoholic solution into 5% ammonia solution we obtained 1.7 g (45%) of (p-chlorophenyl)-p-tolylstibinic acid, which was identified in the form of the double salt



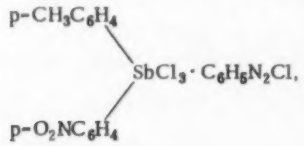
Found %: Sb 20.29; 20.16 $C_{19}H_{15}N_2Cl_6Sb$. Calculated %: Sb 20.10

6. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot ZnCl_2$. To a solution of 1 g (0.003 mole) of dichloro-p-tolylstibine in 15 ml of acetone 2 g (0.006 mole) of $(p\text{-}CH_3OC_6H_4N_2Cl_2) \cdot ZnCl_2$ was added. Reaction proceeded at the boiling point of acetone. The usual treatment gave 1 g of the original double salt $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot ZnCl_2$ and 0.4 g (32%) of (p-methoxyphenyl)-p-tolylstibinic acid, which was identified in the form of the double salt.



Found %: Sb 20.98; 21.22 $C_{21}H_{21}N_2OCl_4Sb$. Calculated %: Sb 20.95

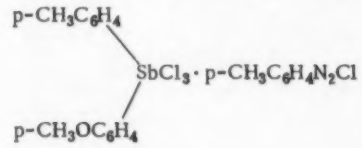
7. Reaction of $p\text{-}CH_3C_6H_4SbCl_2$ with $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 1.5 g (0.0052 mole) of dichloro-p-tolylstibine in 30 ml of acetone, 4 g (0.0096 mole) of $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$ was added gradually at room temperature. After the usual treatment we obtained 1.7 g (87% of (p-nitrophenyl)-p-tolylstibinic acid, which was identified in the form of the double salt



m.p. 74-76° (decomp.).

Found %: Sb 21.28; 21.05 $C_{19}H_{16}N_3O_2Cl_4Sb$. Calculated %: Sb 20.92

8. Reaction of $p\text{-}CH_3C_6H_4SbI_2$ with $p\text{-}CH_3OC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 5 g (0.011 mole) of diiodo-p-tolylstibine in 50 ml of acetone, 5 g (0.012 mole) of $p\text{-}CH_3OC_6H_4N_2Cl \cdot SbCl_3$ was added. When the evolution of of nitrogen ceased in the cold, the mixture was heated at 56° for 30 minutes. The usual treatment was given, and from the ammoniacal solution we isolated 2.5 g (66%) of (p-methoxyphenyl)-p-tolylstibinic acid, which was identified in the form of the double salt



m.p. 99-100° (decomp.)

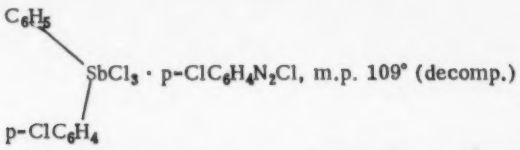
Found %: Sb 21.11; 20.94 $C_{21}H_{21}ON_2Cl_4Sb$. Calculated %: Sb 20.95

9. Reaction of $p\text{-}CH_3C_6H_4SbI_2$ with $p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_3$. To a solution of 6 g (0.013 mole) of diiodo-p-tolylstibine in 50 ml of acetone, 5 g (0.013 mole) of $p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_3$ was added. Reaction went vigorously in the cold. After the usual treatment we obtained 3.1 g (84%) of di-p-tolylstibinic acid, which was identified in the form of the double salt $(p\text{-}CH_3C_6H_4)_2SbCl_3 \cdot p\text{-}CH_3C_6H_4N_2Cl$, m.p. 103-104° (decomp.).

Found %: Sb 21.49; 21.53 $C_{21}H_{21}N_2Cl_4Sb$. Calculated %: Sb 21.55

10. Reaction of $C_6H_5SbCl_2$ with $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 3.5 g (0.013 mole) of dichlorophenylstibine in 25 ml of acetone 6 g (0.015 mole) of $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$ was added. Reaction went vigorously in the

cold. After the usual treatment we obtained 1.5 g (60%) of (p-chlorophenyl)phenylstibinic acid, which was identified in the form of the double salt



C_6H_5

$SbCl_3 \cdot p\text{-}ClC_6H_4N_2Cl$, m.p. 109° (decomp.)

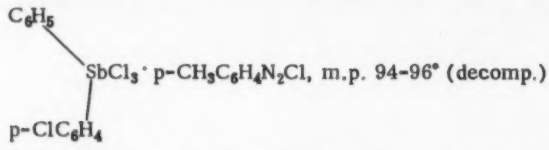
$p\text{-}ClC_6H_4$

Found %: Sb 20.45; 20.55 $C_{18}H_{13}N_2Cl_6Sb$. Calculated %: Sb 20.57

11. Preparation of $p\text{-}ClC_6H_4SbI_2$. 1-Chloro-4-stibosobenzene (10 g; 0.04 mole) was dissolved in 30 ml of glacial acetic acid; the solution was filtered and 10 g (0.06 mole) of potassium iodide was added. When the KI had dissolved completely, concentrated HCl was added until yellow crystals of (p-chlorophenyl)diiodostibine ceased to separate. The yield was 10 g (51%); m.p. 87-89°.

Found %: Sb 25.05; 24.91 $C_6H_4ClI_2Sb$. Calculated %: Sb 25.00

12. Reaction of $p\text{-}ClC_6H_4SbI_2$ with $C_6H_5N_2Cl \cdot SbCl_3$. To the solution of 1.2 g (0.002 mole) of (p-chlorophenyl) diiodostibine in 20 ml of acetone, 1.2 g (0.003 mole) of $C_6H_5N_2Cl \cdot SbCl_3$ was added. When nitrogen ceased to be evolved, the reaction mixture was heated for five minutes at 56°. The usual treatment gave 0.8 g (95%) of (p-chlorophenyl) phenylstibinic acid, which was identified in the form of the double salt



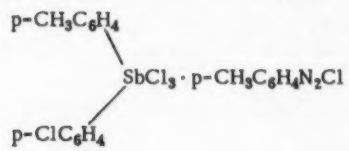
C_6H_5

$SbCl_3 \cdot p\text{-}CH_3C_6H_4N_2Cl$, m.p. 94-96° (decomp.)

$p\text{-}ClC_6H_4$

Found %: Sb 21.13; 21.45 $C_{19}H_{16}N_2Cl_5Sb$. Calculated %: Sb 21.38

13. Reaction of $p\text{-}ClC_6H_4SbI_2$ with $p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_3$. To a solution of 4 g (0.008 mole) of (p-chlorophenyl) diiodostibine in 30 ml of acetone 5 g (0.013 mole) of $p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_3$ was added. When nitrogen ceased to be evolved in the cold, the reaction mixture was heated at 56° for 20 minutes. The product, amounting to 2.5 g (85%), was (p-chlorophenyl)-p-tolylstibinic acid, which was identified in the form of the double salt



$p\text{-}CH_3C_6H_4$

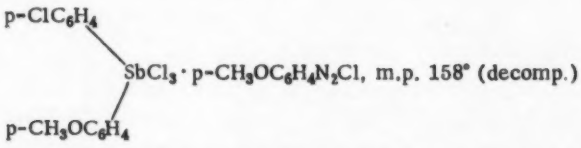
$SbCl_3 \cdot p\text{-}CH_3C_6H_4N_2Cl$

$p\text{-}ClC_6H_4$

m.p. 102° (decomp.)

Found %: Sb 20.76; 20.62 $C_{20}H_{18}N_2Cl_5Sb$. Calculated %: Sb 20.80

14. Reaction of $p\text{-}ClC_6H_4SbI_2$ with $p\text{-}CH_3OC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 6 g (0.012 mole) of (p-chlorophenyl) diiodostibine in 50 ml of acetone, 7 g (0.017 mole) of $p\text{-}CH_3OC_6H_4N_2Cl \cdot SbCl_3$ was added. When nitrogen ceased to be evolved in the cold, the reaction mixture was heated at 56° for ten minutes. The usual treatment gave 0.4 g (9%) of the double salt



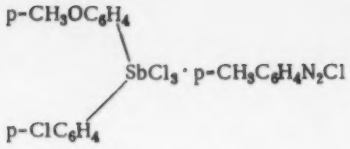
$p\text{-}ClC_6H_4$

$SbCl_3 \cdot p\text{-}CH_3OC_6H_4N_2Cl$, m.p. 158° (decomp.)

$p\text{-}CH_3OC_6H_4$

Found %: Sb 19.83; 19.56 $C_{20}H_{18}O_2N_2Cl_5Sb$. Calculated %: Sb 19.72

From the ammoniacal solution we obtained 3.2 g (69%) of (p-chlorophenyl)(p-methoxyphenyl) stibinic acid, which was identified in the form of the double salt



m.p. 122-124° (decomp.)

Found %: Sb 20.30; 20.22 $C_{20}H_{18}ON_2Cl_5Sb$. Calculated %: Sb 20.25

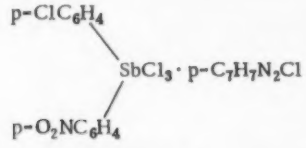
15. Reaction of $p\text{-}ClC_6H_4SbI_2$ with $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$. From 6 g (0.012 mole) of (p-chlorophenyl) diiodostibine and 7 g (0.017 mole) of $p\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$ in acetone in the cold we obtained 0.1 g of tris -p-chlorophenylantimony dichloride, m.p. 190°(the literature [14] gives 193°).

Found %: Sb 23.14; 23.12 $C_{18}H_{12}Cl_5Sb$. Calculated %: Sb 23.07

On addition of the alcoholic solution to ammonia solution we obtained 4 g (86%) of bis-p-chlorophenylstibinic acid, which was identified in the form of $(p\text{-}ClC_6H_4)_2SbCl_3 \cdot p\text{-}CH_3C_6H_4N_2Cl$, m.p. 101° (decomp.).

Found %: Sb 20.28; 20.04 $C_{19}H_{15}N_2Cl_6Sb$. Calculated %: Sb 20.10

16. Reaction of $p\text{-}ClC_6H_4SbI_2$ with $p\text{-}O_2NC_6H_4N_2Cl_3SbCl_3$. From 4.6 g (0.009 mole) of (p-chlorophenyl) diiodostibine and 4.6 g (0.011 mole) of $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$ in 30 ml of acetone under the conditions of the previous experiment we obtained 4 g of (p-chlorophenyl)(p-nitrophenyl) stibinic acid contaminated with resinous material. The acid was identified in the form of the double salt



m.p; 103-104° (decomp.)

Found %: Sb 19.90; 19.78 $C_{19}H_{15}O_2N_3Cl_5Sb$. Calculated %: Sb 19.75

17. Reaction of $(C_6H_5)_2SbOCOCH_3$ with $C_6H_5N_2OCOCH_3$. a) To a solution of 3 g (0.009 mole) of acetoxydiphenylstibine in 75 ml of acetone, 1.5 g (0.009 mole) of benzenediazoacetate was added. The reaction went at room temperature, but in order to complete it the reaction mixture was heated at 56° for five minutes. The reaction mixture was set aside for one day in a closed flask, 0.9 g of a precipitate of triphenylantimony diacetate formed. Removal of solvent by distillation gave a further 0.45 g of this substance. After two crystallizations from glacial acetic acid the substance had m.p 204-205°.

Found %: C 52.92; 52.86; H 4.41; 4.41 $(C_6H_5)_3Sb(OCOCH_3)_2 \cdot 2CH_3COOH$. Calculated %: C 52.81; H 4.91

The total yield was 1.35 g (26%). By treatment with alcoholic HCl, the triphenylantimony diacetate was converted into triphenylantimony dichloride, m.p. 142-143° (the literature [2] gives 143°).

b) A solution of 1 g (0.003 mole) of acetoxydiphenylstibine in 25 ml of acetone was heated to the boil, and 1 g (0.006 mole) of benzenediazoacetate was added gradually. Solvent was evaporated off, and the residual thick mass was treated with a little alcoholic HCl. The precipitate was filtered off and dissolved in the minimum amount of chloroform. The solution was filtered, and alcohol was added. The product, amounting to 0.5 g (40%), was triphenylantimony dichloride, m.p. 142-143° (the literature [2] gives 143°).

18. Reaction of $(p\text{-}CH_3C_6H_4)_3SbOCOCH_3$ with $p\text{-}CH_3C_6H_4N_2OCOCH_3$. To a solution of 3 g (0.0083 mole) of acetoxydi-p-tolylstibine in 75 ml of acetone 3 g (0.017 mole) of p- tolyldiazoacetate was added. To start reaction the mixture was heated to the boil, and the reaction then went with evolution of heat and was complete in 15-20 minutes. After the usual treatment of precipitate of $(C_7H_7)_3Sb(OH)(OCOCH_3)$ separated from alcohol. The yield was 2.6 g (59%). After two crystallizations from glacial acetic acid it had m.p. 166-167° (the literature gives 168-169° [15] and 165° [16]).

Found %: Sb 26.01; 26.17 $C_{23}H_{25}O_3Sb$. Calculated %: Sb 25.84

19. Preparation of $(o\text{-}ClC_6H_4)_2SbCl$. 1-Chloro-2-stibosobenzene (5.6 g), prepared by the double diazonium salt method [2], was ground with 6 ml of concentrated HCl. The resulting crystals of chlorobis-o-chlorophenylstibine • were crystallized from glacial acetic acid; m.p. 94-95°.

Found %: C 38.11; 38.00; H 2.47; 2.30 $C_{12}H_8Cl_3Sb$. Calculated %: C 37.89; H 2.12

20. Reaction of $(o\text{-}ClC_6H_4)_2SbCl$ with $o\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 2.5 g (0.0065 mole) of chlorobis-o-chlorophenylstibine in 40 ml of acetone, 4 g (0.01 mole) of $o\text{-}ClC_6H_4N_2Cl \cdot SbCl_3$ was added. The reaction was exothermic and was complete in 30-35 minutes. Solvent was distilled off, and after the usual treatment 2.5 g (73%) of tris-o-chlorophenylantimony dichloride was isolated from alcohol. After crystallization from acetone it had m.p. 204-206° (the literature [9] gives 205-206°). There was no depression of melting point in admixture with known $(o\text{-}ClC_6H_4)_3SbCl_2$.

21. Reaction of $(o\text{-}ClC_6H_4)_2SbCl$ with $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$. From 3.8 g (0.01 mole) of chlorobis-o-chlorophenylstibine and 6 g (0.0147 mole) of $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$ in 50 ml of acetone under the conditions of the previous experiment we obtained 2.4 g (45%) of bis-o-chlorophenyl(p-nitrophenyl) antimony dichloride. The substance was crystallized from benzene; m.p. 202°.

Found %: C 40.06; H 2.35; 2.25; N 2.93; 2.96 $C_{18}H_{12}O_2Cl_4Sb$. Calculated %: C 40.19; H 2.25; N 2.60

22. Reaction of $(o\text{-}C_2H_4OC_6H_4)_2SbCl$ with $(o\text{-}ClC_6H_4N_2Cl)_2ZnCl_2$. To a solution of 5 g (0.0125 mole) of chlorobis-o-ethoxyphenylstibine •• in 80 ml of acetone at room temperature, 4 g (0.008 mole) of $(o\text{-}ClC_6H_4N_2Cl)_2\text{-}ZnCl_2$ was added. As a result of the usual treatment (o-chlorophenyl)bis-o-ethoxyphenylantimony dichloride was isolated from alcohol. The yield was 5.1 g (74%); m.p. 188-189°, raised by crystallization from a mixture of chloroform and alcohol to 189-190°.

Found %: C 48.76; 48.53; H 4.42; 4.31 $C_{22}H_{22}O_2Cl_3Sb$. Calculated %: C 48.34; H 4.24

23. Reaction of $(o\text{-}C_2H_5OC_6H_4)_2SbCl$ with $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$. To a solution of 4.5 g (0.011 mole) of chlorobis-o-ethoxyphenylstibine in 75 ml of acetone 10.5 g (0.025 mole) of $p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_3$ was added gradually at room temperature. Reaction occurred with evolution of much heat. During the reaction a precipitate was formed of bis-o-ethoxyphenyl(p-nitrophenyl)antimony dichloride, which was filtered off when reaction was complete and was washed with 5 N HCl. The substance formed colorless crystals, readily soluble in chloroform, moderately soluble in cold acetone and benzene, and sparingly soluble in alcohol; m.p. 230° yield 1 g.

Found %: C 47.35; 47.13; H 3.91; 3.69; N 2.69; 2.75 $C_{22}H_{22}O_4NCl_2Sb$. Calculated %: C 47.42; H 3.93; N 2.51

Solvent was distilled off, and the usual treatment gave a further 4.2 g of bis-o-ethoxyphenyl(p-nitrophenyl) antimony dichloride, m.p. 227-228°, undepressed by admixture of the substance obtained earlier.

Found %: C 47.32; 47.64; H 4.07; 4.04; N 2.77; 2.74 $C_{22}H_{22}O_4NCl_2Sb$. Calculated %: C 47.42; H 3.93; N 2.51

The total yield of bis-o-ethoxyphenyl(p-nitrophenyl)antimony dichloride was 5.2 g (82%).

SUMMARY

1. The arylation of organoantimony compounds of the types $ArSbX_2$ and Ar_2SbX with diazo compounds was studied.

• Under the conditions of the reaction dichloro(o-chlorophenyl)stibine undergoes disproportionation, as a result of which the product is $(o\text{-}ClC_6H_4)_2SbCl$, and not $o\text{-}ClC_6H_4SbCl_2$ as would be expected.

•• $(o\text{-}C_2H_5OC_6H_4)_2SbCl$ was prepared by the double diazonium salt method [2]; m.p. 107-108°.

Found %: C 47.98; 47.97; H 4.70; 4.70 $C_{16}H_{18}O_2ClSb$. Calculated %: C 48.08; H 4.54

This compound was previously [2] taken to be $o\text{-}C_2H_5OC_6H_4SbCl_2$.

2. The most convenient method for the preparation of compounds of the type $ArAr'SbX_3$ is the reaction of aryldiiodostibines with double diazonium-antimony chlorides.

3. A method was developed for the synthesis of compounds of the type $Ar_2Ar'SbX_2$ by reaction of Ar_2SbX with aryldiazoacetates or double diazonium-metal chlorides.

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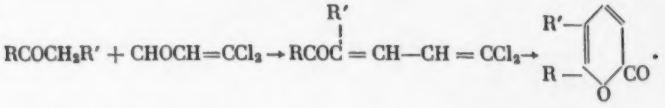
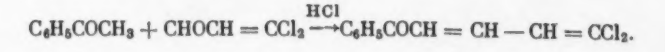
CONDENSATION OF 3,3-DICHLOROACROLEIN WITH CARBONYL COMPOUNDS AND CONVERSION OF THE CONDENSATION PRODUCTS INTO 2H-PYRAN-2-ONE DERIVATIVES

L. I. Zakharkin and L. P. Sorokina

3,3-Dichloroacrolein $CCl_2=CH-CHO$, which has recently become readily accessible [1], has various potentialities in the synthesis of compounds containing the $CCl_2=CH$ group. In the present investigation we studied the condensation of 3,3-dichloroacrolein with some carbonyl compounds with formation of dichloro dienic ketones and examined the possibility of cyclizing these products into 2H-pyran-2-one derivatives:

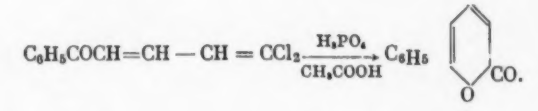


With aliphatic-aromatic ketones the reaction of 3,3-dichloroacrolein proceeds readily in presence of hydrogen chloride. Thus, with acetophenone 3,3-dichloroacrolein gives 5,5-dichloro-2,4-pentadienophenone:

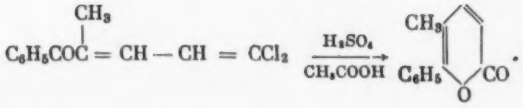


4'-Chloroacetophenone, 4'-hydroxyacetophenone, propiophenone, and butyrophenone react similarly.

The use of bases as catalysts in this reaction, even such weak bases as potassium acetate, is excluded, because they bring about the elimination of HCl from 3,3-dichloroacrolein. When 5,5-dichloro-2,4-pentadienophenone is heated in glacial acetic acid solution in presence of a little sulfuric or, better, phosphoric acid, hydrogen chloride is liberated and 6-phenyl-2H-pyran-2-one is formed in good yield:



When concentrated sulfuric acid is used as medium the yield of 6-phenyl-2H-pyran-2-one is much lower as a result of resinification and, probably, sulfonation of the benzene ring. In a similar way the following are readily converted into the corresponding 2H-pyran-2-one derivatives: 4'5,5-trichloro-2,4-pentadienophenone and 5,5-dichloro-4'-hydroxy-2,4-pentadienophenone. The formation of 5-methyl-6-phenyl-2H-pyran-2-one from 5,5-dichloro-2-methyl-2,4-pentadienophenone proceeds much less readily and only in the presence of sulfuric acid:



The product of the condensation of 3,3-dichloroacrolein with butyrophenone behaves differently from the dichloropentadienophenones referred to above. It is a liquid which, when heated in glacial acetic acid solution in presence of sulfuric acid, does not give a 2H-pyran-2-one derivative, but is converted into a crystalline compound (m.p. 68-69°) of the same composition as the original 5,5-dichloro-2-ethyl-2,4-pentadienophenone. Both compounds, liquid and solid, form 2,4-dinitrophenylhydrazones, which differ in melting point and have depressed melting points in admixture. It may be supposed that the two compounds are cis-trans isomers and that isomerization of the liquid isomer into the solid isomer occurs with heating in an acid medium. When the liquid isomer is heated in concentrated sulfuric acid solution a 2H-pyran-2-one derivative is again not formed, but the $CCl_2=$ CH group is hydrolyzed with formation of an acid:

$$C_6H_5COC(C_2H_5)=CH-CH=CCl_2 \xrightarrow[H_2O]{H_2SO_4} C_6H_5COC(C_2H_5)=CH-CH_2COOH.$$

It was not found possible to obtain the condensation product in the reaction of acetone with 3,3-dichloroacrolein because only resins were formed.

In the condensation of butanone with 3,3-dichloroacrolein in presence of hydrogen chloride low yields were obtained of a substance that was probably 6,6-dichloro-3-methyl-3,5-hexadien-2-one:

$$CH_3COCH_2CH_3 + CHOCH=CCl_2 \xrightarrow{HCl} CH_3COC(CH_3)=CH-CH=CCl_2.$$

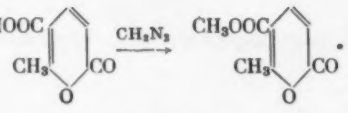
6,6-Dichloro-3-methyl-3,5-hexadien-2-one could not be converted into a 2H-pyran-2-one derivative: heating in acid media led to rapid resinification.

In presence of dry hydrogen chloride acetoacetic ester readily reacted with 3,3-dichloroacrolein with formation of ethyl 2-(3,3-dichloroallylidene)acetoacetate:

$$CH_3COCH_2COOC_2H_5 + CHOCH=CCl_2 \xrightarrow{HCl} CH_3COC(COOC_2H_5)=CH-CH=CCl_2.$$

This substance is very unstable to heat and can be distilled only in a high vacuum. When heated for a short time in water bath it is converted into products that cannot be vacuum-distilled without decomposition. With 2,4-dinitrophenylhydrazine it readily forms a 2,4-dinitrophenylhydrazone. When allowed to stand for a few days ethyl 2-(3,3-dichloroallylidene)acetoacetate is partially converted into a crystalline substance of composition $C_7H_6O_4$ with liberation of hydrogen chloride. This compound was found to be 6-methylcoumalic acid; its structure was proved by conversion into the known methyl 6-methylcoumalate:

$$CH_3COC(COOC_2H_5)=CH-CH=CCl_2 \rightarrow$$

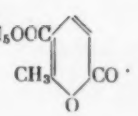


$$\xrightarrow{CH_2N_2}$$

It may be considered that the formation of 6-methylcoumalic acid results from cyclization of the dichloropentadiene system in presence of moisture and subsequent hydrolysis of the ester grouping.

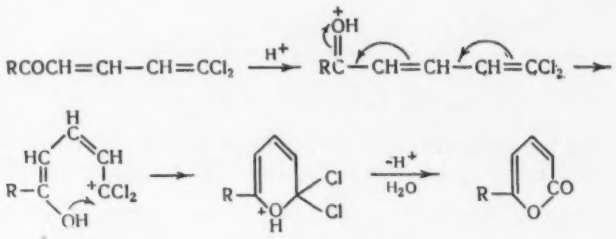
Heating of ethyl 2-(3,3-dichloroallylidene)acetoacetate in glacial acetic acid solution in presence of a little hydrochloric acid results in the formation in low yield of a compound of composition $C_9H_{10}O_4$, which appears to be ethyl 6-methylcoumalate:

$$CH_3COC(COOC_2H_5)=CH-CH=CCl_2 \xrightarrow[CH_3COOH]{HCl}$$



Unlike 2,3,3-trichloroacrolein [2], 3,3-dichloroacrolein reacts with dimedone in the usual way, i.e. one molecule of the aldehyde reacts with two molecules of dimedone.

As regards the mechanism of the cyclization of the dichloropentadiene system into the 2H-pyran-2-one system, we may suppose that the dichlorovinyl group is hydrolyzed in an acid medium to a carboxy group and the keto acid formed undergoes cyclization. In this case addition of a proton to the $CCl_2=CH$ group would occur in the hydrolysis, but it is more probable that the proton will add at the end of the conjugated system, i.e. to the carbonyl oxygen, in which case the cyclization can be represented as follows:



EXPERIMENTAL

5,5-Dichloro-2,4-pentadienophenone. A mixture of 10 g of 3,3-dichloroacrolein and 11.5 g of acetophenone was saturated with dry hydrogen chloride for one hour under cooling with ice water. The mixture was left overnight and had crystallized almost completely by the next day. The crystals were filtered off from the small residue of liquid. Recrystallization from alcohol gave 13.7 g (76%) of 5,5-dichloro-2,4-pentadienophenone, m.p. 76-77°.

Found %: C 58.22; 58.08; H 3.57; 3.32; Cl 31.06; 29.64 $C_{11}H_8Cl_2O$. Calculated %: C 58.19; H 3.55 Cl 31.23

The 2,4-dinitrophenylhydrazone had m.p. 215-215.5° (from acetic acid).

Found %: N 13.82; 13.96 $C_{17}H_{12}N_4Cl_2O_4$. Calculated %: N 13.69

5,5-Dichloro-2,4-pentadienophenone reacts with one molecular proportion of bromine with formation of a dibromide of composition $C_{11}H_8Br_2Cl_2O$.

Found %: C 34.14; 34.35; H. 2.12; 2.16 $C_{11}H_8Br_2Cl_2O$. Calculated % C 34.12; H 2.06

4',5,5-Trichloro-2,4-pentadienophenone. A mixture of 10 g of 3,3-dichloroacrolein and 13.5 g of 4'-chloroacetophenone was saturated with dry hydrogen chloride for one hour under cooling with ice water. In the course of this process the reaction mixture crystallized out completely. The reaction product was recrystallized from alcohol, and we obtained 15.5 g (75%) of 4'5,5-trichloro-2,4-pentadienophenone, m.p. 122°.

Found %: C 50.88; H 2.86; Cl 40.42 $C_{11}H_7Cl_3O$. Calculated %: C 50.49; H 2.67; Cl 40.71

5,5-Dichloro-4'-hydroxy-2,4-pentadienophenone. A mixture of 5.3 g of 3,3-dichloroacrolein and 6 g of 4'-hydroxyacetophenone in 35 ml of glacial acetic acid was saturated with dry hydrogen chloride for one hour under cooling with ice water. After three days the small residue of 4'-hydroxyacetophenone was filtered off, and the acetic acid solution was poured into water. The precipitate that formed was filtered off; yield of unpurified reaction product 8.3 g (80%). After numerous crystallizations from aqueous alcohol (with treatment with activated charcoal) 5,5-dichloro-4'-hydroxy-2,4-pentadienophenone melted at 156-157°.

Found %: C 54.37; 54.57; H 3.37; 3.39; Cl 28.90 $C_{11}H_8Cl_2O_2$. Calculated %: C 54.34; H 3.29 Cl 29.20

5,5-Dichloro-2-methyl-2,4-pentadienophenone. A mixture of 13.8 g of 3,3-dichloroacrolein and 16.5 g of propiophenone was satureated with dry hydrogen chloride for 80 minutes under cooling with ice water. After a few hours the reaction mixture crystallized completely. Recrystallization from alcohol gave 20.7 g (77%) of 5,5-dichloro-2-methyl-2,4-pentadienophenone, m.p. 82-83°.

Found %: C 59.76; 59.91; H 4.33; 4.13; Cl 29.30; 29.28 $C_{12}H_{10}Cl_2O$. Calc. %: C 59.76; H 4.14; Cl 29.44;

5,5-Dichloro-2-ethyl-2,4-pentadienophenone. A mixture of 10 g of 3,3-dichloroacrolein and 14.1 g of butyrophenone was saturated with dry hydrogen chloride for 90 minutes under cooling with ice water and was left for 48 hours. It was then poured into water, and the oil liberated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. Chloroform was distilled off, and vacuum distillation of the reaction product gave 16.1 g (78%) of 5,5-dichloro-2-ethyl-2,4-pentadienophenone; b.p. 144-145° (2 mm); $n^{20}D$ 1.5958; d^{20}_4 1.2088.

Found %: C 61.52; 61.43; H 4.54; 4.73; Cl 27.14; 27.30 $C_{13}H_{12}Cl_2O$. Calculated %: C 61.19; H 4.70 Cl 27.83

Its 2,4-dinitrophenylhydrazone had m.p. 146-148° (from alcohol).

Found %: N 12.54; 12.52 $C_{19}H_{16}N_4Cl_2O_4$. Calculated %: N 12.86

In the course of standing for two months a crystalline solid, m.p. 181-182° (from alcohol), separated from 5,5-dichloro-2-ethyl-2,4-pentadienophenone; its analysis was C 67.33; 67.27; H 5.49; 5.46; Cl 15.15; 15.33%.

6-Phenyl-2H-pyran-2-one. A mixture of 4 g of 5,5-dichloro-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 1 ml of 94% sulfuric acid was boiled for five hours. The reaction mixture was poured into water, and the oil liberated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. The oil that remained after removal of chloroform solidified after a short time. We obtained 1.7 g (57%) of 6-phenyl-2H-pyran-2-one. After crystallization from petroleum ether it had m.p. 67° (the literature [3] gives 68°).

Found %: C 77.19; 77.27; H 4.68; 4.62 $C_{11}H_8O_2$. Calculated %: C 76.73; H 4.67

A mixture of 4 g of 5,5-dichloro-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 1 ml of phosphoric acid was boiled for 17 hours. Treatment of the reaction mixture as described above gave 2.1 g (70%) of 6-phenyl-2H-pyran-2-one.

When the reaction was carried out in concentrated sulfuric acid or in acetic acid with addition of concentrated perchloric acid, much resinification occurred and the yields of6-phenyl-2H-pyran-2-one were much lower.

6-p-Chlorophenyl-2H-pyran-2-one. A mixture of 4 g of 4',5,5-trichloro-2,4-pentadienophenone, 20 ml of glacial acetic acid, and 1 ml of 94% sulfuric acid was boiled for 16 hours. The reaction mixture was then poured into water, and the crystalline precipitate formed was filtered off. We obtained 2.3 g (75%) of unpurified 6-p-chlorophenyl-2H-pyran-2-one, which was purified by dissolution in ether, subsequent removal of ether by distillation, and crystallization from petroleum ether; m.p. 93-94°.

Found %: C 63.71; 63.71; H 3.32; 3.49; Cl 17.08 $C_{11}H_7ClO_2$. Calculated %: C 63.94; H 3.38; Cl 17.18

A mixture of 4 g of 4'5,5-trichloro-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 1 ml of 88% phosphoric acid was boiled for 16 hours. We obtained 3.2 g (100%) of 6-p.chlorophenyl-2H-pyran-2-one.

6-p-Hydroxyphenyl-2H-pyran-2-one. A mixture of 3.6 g of 5,5-dichlor-4'-hydroxy-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 2 ml of 88% phosphoric acid was boiled for 20 hours. The reaction mixture was poured into water, and the precipitate formed was filtered off. The yield of unpurified product was 3.1 g. After several crystallizations from water, it melted at 222-223°.

Found %: C 70.12; 69.93; H 4.28; 4.30 $C_{11}H_8O_3$. Calculated %: C 70.22; H 4.25

5-Methyl-6-phenyl-2H-pyran-2-one. A mixture of 4 g of 5,5-dichloro-2-methyl-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 1.5 ml of 94% sulfuric acid was boiled for 24 hours. The reaction mixture was poured into water, and the oil that separated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. Chloroform was distilled off, and vacuum distillation of the residue gave 2.4 g of oil, b.p. 135-136° (2 mm). On the next day the oil began to crystallize. The crystals were filtered off and were recrystallized from alcohol. The melting point of 5-methyl-6-phenyl-2H-pyran-2-one was 98-99°.

Found %: C 77.54; 77.36; H 5.47; 5.46 $C_{12}H_{10}O_2$. Calculated %: C 77.43; H 5.37

A mixture of 4 g of liquid 5,5-dichloro-2-ethyl-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 2 ml of 94% sulfuric acid was boiled for 28 hours. The reaction mixture was poured into water, and the oil that separated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. Chloroform was distilled off, and the oil crystallized. We obtained 2.9 g of crystalline 5,5-dichloro-2-ethyl-2,4-pentadienophenone, m.p. 68-69° (from alcohol).

Found %: C 61.44; 61.65; H 4.69; 4.85; Cl 28.04; 27.92 $C_{13}H_{12}Cl_2O$. Calculated %: C 61.19; H 4.70; Cl 27.83

Its 2,4-dinitrophenylhydrazone had m.p. 177-177.5° (from acetic acid).

Found %: N 12.66; 12.51 $C_{19}H_{16}N_4Cl_2O_4$. Calculated %: N 12.86

A mixture of this dinitrophenylhydrazone with that of liquid 5,5-dichloro-2-ethyl-2,4-pentadienophenone melted at 130-135°.

4-Benzoyl-3-hexenoic Acid. A mixture of 10 g of 5,5-dichloro-2-ethyl-2,4-pentadienophenone and 10 ml of 94% sulfuric acid was heated for 12 hours at 110-120°. The reaction mixture was poured into water, and the oil that separated was extracted with chloroform. The chloroform solution was extracted with sodium hydroxide solution, which was then acidified; an oil separated and was extracted with chloroform. The chloroform solution, neutral and acid, were dried over calcium chloride. No neutral reaction products were found when chloroform was distilled from the first solution. Distillation of chloroform from the acid solution gave a low yield of 4-benzoyl-3-hexenoic acid, b.p. 190-191° (2 mm).

Found %: C 71.55; 71.66; H 6.46; 6.47; $C_{13}H_{14}O_3$. Calculated %: C 71.57; H 6.41

The 2,4-dinitrophenylhydrazone had m.p. 142.5-143.5° (from acetic acid).

6,6-Dichloro-3-methyl-3,5-hexadien-2-one. A mixture of 10 g of 3,3-dichloroacrolein and 7.1 g of butanone was saturated with dry hydrogen chloride for 20 minutes under cooling with ice water. The mixture was left overnight, and on the next day it was poured into water, and the oil that separated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. Chloroform was distilled off, and vacuum distillation gave 4 g (30%) of 6,6-dichloro-3-methyl-3,5-hexadien-2-one, b.p. 77-78° (3 mm) and m.p. 24.5-25.5° (from petroleum ether).

Found %: C 46.90; 46.99; H 4.44; 4.43; Cl 39.41 C_7H_8ClO. Calculated %: C 46.94; H 4.46; Cl 39.64

When 6,6-dichloro-3-methyl-3,5-hexadien-2-one was boiled in glacial acetic acid and when it was heated at 70° in presence of 94% sulfuric acid there was considerable resinification and only unchanged 6,6-dichloro-3-methyl-3,5-hexadien-2-one was isolated.

Ethyl 2-(3,3-Dichloroallylidene) acetoacetate. A mixture of 10 g of 3,3-dichloroacrolein and 9.4 g of ethyl acetoacetate was saturated with dry hydrogen chloride for 90 minutes under cooling with ice water. The mixture was left overnight, and on the next day it was poured into water, and the oil that separated was extracted with ether. The ether solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. The removal of ether left 15.9 g (87%) of undistilled reaction product. The product was distilled in a high vacuum; $n^{20}D$ 1.5381; d^{20}_4 1.2520.

Found %: C 45.48; 45.41; H 4.30; 4.22; Cl 30.26; 30.15 $C_9H_{10}Cl_2O_3$. Calculated %: C 45.59; H 4.21; Cl 29.98

Its 2,4-dinitrophenylhydrazone had m.p. 153-154° (from acetic acid).

Found %: C 43.17; 43.24; H 3.35; 3.49; N 13.45; 13.47 $C_{15}H_{14}N_4Cl_2O_6$. Calculated %: C 43.18; H 3.38; N 13.42

In the course of standing for three months, crystalline 6-methylcoumalic acid, m.p. 182.5° (from benzene), separated from the ethyl 2-(3,3-dichloroallylidene)acetoacetate.

Found %: C 54.43; 54.34; H 3.98; 4.06 $C_7H_6O_4$. Calculated % C 54.54; H 3.90

To prove the structure of the 6-methylcoumalic acid we converted it into its methyl ester by the action of diazomethane; the product had m.p. 84° (from petroleum ether), undepressed by admixture of methyl 6-methylcoumalate synthesized from methyl coumalate [4].

Ethyl 6-Methylcoumalate. A mixture of 22 g of ethyl 2-(3,3-dichloroallylidene) acetoacetate, 50 ml of glacial acetic acid, and 1.5 ml of concentrated HCl was boiled for seven hours. When cool, the reaction mixture was poured into water. The mixture was extracted with ether, and the ether solution was washed with sodium carbonate solution and with water; it was dried over calcium chloride. Ether was distilled off, and vacuum distillation of the residue gave 4 g (25%) of ethyl 6-methylcoumalate; b.p. 114-115° (2 mm); $n^{20}D$ 1.5197; d^{20}_4 1.1973; found M.W. 177.2 (cryoscopic determination in benzene); calculated M.W. 182.1.

Found %: C 59.28; 59.15; H 5.84; 5.78 $C_9H_{10}O_4$. Calculated %: C 59.34; H 5.47

Condensation of 3,3-Dichloroacrolein with Dimedone. A mixture of 0.9 g of 3,3-dichloroacrolein and 2 g of dimedone was heated in 100 ml of 50% ethanol for one hour in a water bath at 70-80°. In the course of the heating a crystalline precipitate began to form. After two days the crystals were filtered off. The reaction product, which amounted to 1.6 g (60%), was insoluble in alkali, and a test with $FeCl_3$ was negative; m.p. 158-159° (from aqueous alcohol).

Found %: C 61.72; H 6.05 $C_{19}H_{22}Cl_2O_3$. Calculated %: C 61.77; H 6.00

The condensation of 3,3-dichloroacrolein with 1,3-cylcohexanedione gave a similar product, m.p. 203.5-204° (from aqueous alcohol).

Found %: C 57.13; 57.28; H 4.29; 4.57; Cl 22.27; 22.25 $C_{15}H_{14}Cl_2O_3$. Calculated %: C 57.51; H 4.50; Cl 22.66

SUMMARY

1. A study was made of the condensation of 3,3-dichloroacrolein with various ketones; the products were substituted 5,5-dichloro-2,4-pentadien-1-ones.

2. These substituted 5,5-dichloro-2,4-pentadien-1-ones are cyclized in an acid medium with formation of 2H-pyran-2-one derivatives.

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DECOMPOSITION OF ARYLDIAZONIUM FLUOBORATES IN NITROBENZENE

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In previous investigations the heterolytic character of the decomposition of benzenediazonium fluoborate [1] and of benzenediazonium fluosilicate [2] was proved in reactions of oriented substitution in the benzene nucleus. It was shown that, unlike aryl radicals, which attack mainly in positions ortho and para to any substituent in the benzene nucleus (see, e.g [3-6]), phenyl generated by the decomposition of these diazonium salts in a monosubstituted benzene containing an orientator "of the second kind" (i.e. normally meta-directing) enters this benzene derivative (e.g nitrobenzene) in the meta position. The 3-nitrobiphenyl formed by decomposition in nitrobenzene was isolated from the reaction mixture by fractional distillation and crystallization.

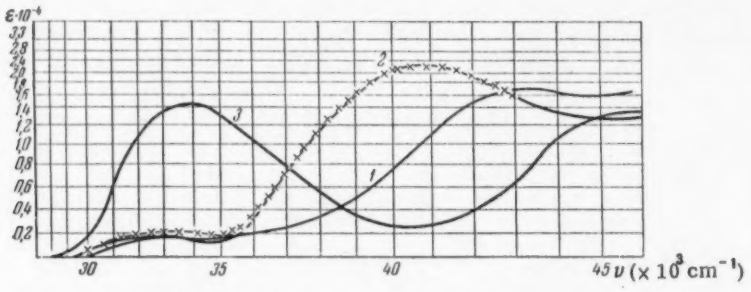


Fig. 1. Absorption curves of solutions in isooctane: 1) 2-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); 2) 3-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); 3) 4-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); x – product of the decomposition of benzenediazonium fluoborate in nitrobenzene (0.06 g/liter).

We have now investigated the decomposition of benzene-, p-toluene-, p-chlorobenzene-, p-anisole-, o-(methoxycarbonyl)benzene-, p-(ethoxycarbonyl)benzene-, o-nitrobenzene-, and o-chlorobenzene-diazonium fluoborates in nitrobenzene. Apart from methods based on the direct separation of the reaction products by fractionation and crystallization, absorption spectroscopy was used in the analysis of the products to determine the relative amounts of o-, m-, and p-isomers formed. In the first six of the cases investigated, the aryl formed by the decomposition of the aryldiazonium fluoborate in nitrobenzene entered the nitrobenzene nucleus exclusively in the m-position, as was expected. Of the three possible isomers (ortho, meta, and para) we isolated only one: the corresponding 3-nitrobiaryl.

Analysis of the crude products of the reactions of these aryldiazonium fluoborates with nitrobenzene (after separation from light fractions) by means of ultraviolet spectroscopy confirmed the presence of only m-isomers in these mixture. Figures 1-6 give the absorption curves of isooctane solutions of the unpurified reaction products and of the corresponding isomeric nitrobiaryls (Figures 1-4, thickness of layer of solution 0.1 cm; Figures 5 and 6 thickness of layer 0.4 cm). The absorption curves were determined with the SF-4 spectrophotometer designed by V. I. Dianov-Klokov.*

* The authors express their warm thanks to I. V. Obreimov and I. Kachkurova for carrying out the spectroscopic measurements.

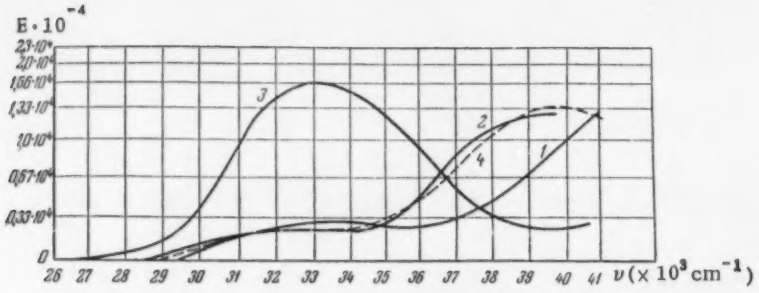


Fig. 2. Absorption curves of solutions in isooctane: 1) 4'-methyl-2-nitrobiphenyl ($3 \cdot 10^{-3}$ mole/liter); 2) 4'methyl-3-nitrobiphenyl ($3 \cdot 10^{-3}$ mole/liter); 3) 4-methyl-4'-nitrobiphenyl ($5 \cdot 10^{-3}$ mole/liter); 4) product of the decomposition of p-toluenediazonium fluoborate in nitrobenzene ($6 \cdot 10^{-4}$ g/liter).

As will be seen from Figures 1-6, the absorption curves of the reaction products almost coincide with those of the corresponding 3-nitrobiaryls, which makes it unnecessary to make the usual calculations from the spectroscopic measurements in order to determine the contents of o-, m-, and p-isomers in the reaction mixture.

The yields of 3-nitrobiaryls formed in the reactions studied were low. As a result of simultaneous spontaneous thermal decomposition of the aryldiazonium fluoborate by Balz and Schiemann's reaction, another product was always the aryl fluoride. The decomposition of aryldiazonium fluoborates in nitrobenzene was accompanied

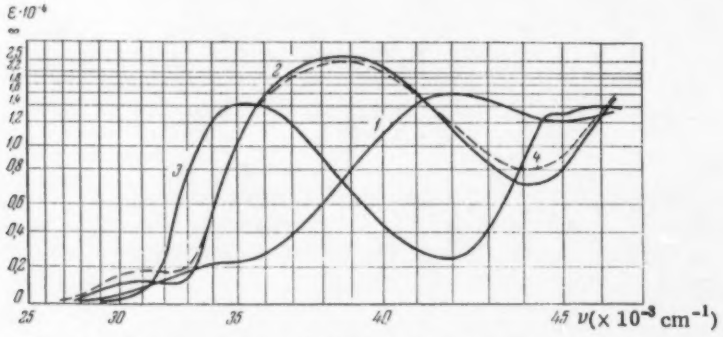


Fig. 3. Absorption curves of solutions in isooctane: 1) 4'-methoxy-2-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); 2) 4'methoxy-3-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); 3) 4-methoxy-4'-nitrobiphenyl ($3 \cdot 10^{-4}$ mole/liter); 4) product of the decomposition of p-anisolediazonium fluoborate in nitrobenzene (0.069 g/liter).

also by the formation of considerable amounts of black tar, which was partially soluble in alkali and contained boron and fluorine. In spite of the very low yields and the occurrence of these reactions of aryl fluoride and tar formation, which, from our point of view, were side reactions, the general picture of the reaction in which we were interested emerged with sufficient clarity. The aryls phenyl, p-tolyl, p-chlorophenyl, p-methoxyphehyl, p-(ethoxycarbonyl)phenyl, o-(methoxycarbonyl)phenyl formed in the decomposition of the corresponding aryldiazonium fluoborates in nitrobenzene, entered the position meta to the nitro group, whereas the aryl radicals formed in the decomposition of the homolytically decomposing aryldiazohydroxides [3, 4, 7], aryldiazoacetates [4], dialkylaryltriazenes [8], and diaroyl peroxides [5, 6] enter the nitrobenzene nucleus in the o- and p-position and do not usually give more than 11% of the m-isomer (according to spectrographic analysis). Other radicals, e.g. the OH radical, also enter the o- and p-positions in nitrobenzene [9].

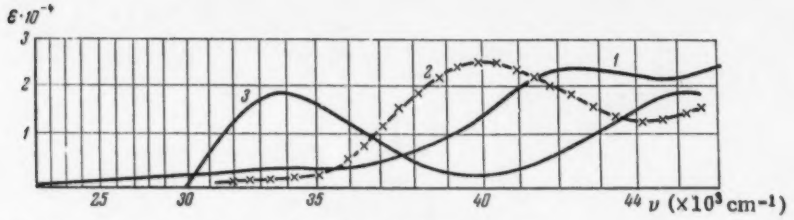


Fig. 4. Absorption curves of solutions in isooctane: 1) 4'-chloro-2-nitrobiphenyl ($1 \cdot 10^{-4}$ mole/liter); 2) 4'-chloro-3-nitrobiphenyl ($1 \cdot 10^{-4}$ mole/liter); 3) 4-chloro-4'-nitrobiphenyl ($1 \cdot 10^{-4}$ mole/liter); x– product of the decomposition of p-chlorobenzenediazonium fluoborate in nitrobenzene (0.0234 g/liter).

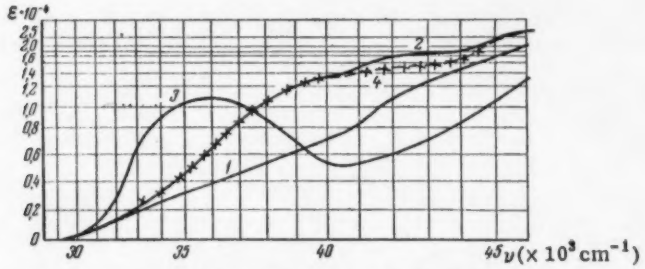
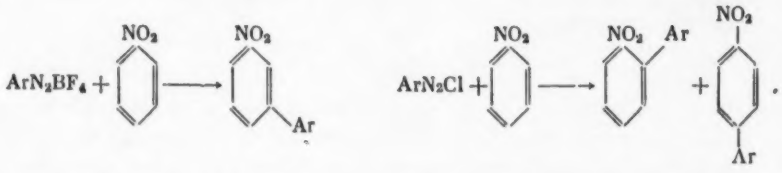


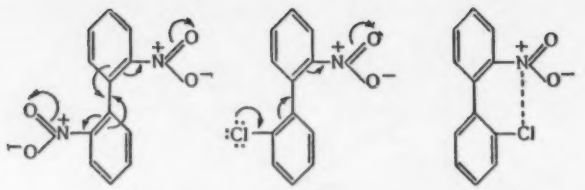
Fig. 5. Absorption curves of solutions in isooctane: 1) methyl 2'-nitro-2-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 2) methyl 3'-nitro-2-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 3) methyl 4'-nitro-2-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 4) product of the decomposition of o-(methoxycarbonyl)benzenediazonium fluoborate in nitrobenzene (0.0257 g/liter).

Hence, the behavior of these aryls derived from aryldiazonium fluoborates in the reaction with nitrobenzene differs from the behavior of aryl radicals:



The entry of the aryl derived from an aryldiazonium fluoborate in the m-position in nitrobenzene, in accordance with the orienting effect of an orientator of the second kind, proves the electrophilic, cationic character of this aryl and the heterolytic nature of the decomposition of the diazonium salt from which the aryl is derived.

Only in two of the cases that we investigated (in the decomposition of o-nitro- and o-chloro-benzenediazonium fluoborates in nitrobenzene) did the aryl unexpectedly enter the o-position in nitrobenzene. In these two cases the only biphenyl derivatives isolated were 2,2'-dinitro- and 2-chloro-2'-nitro-biphenyls, respectively. In the first case the formation of 2,2'-dinitrobiphenyl may be the result of crossed conjugation of the two nitro groups with the two benzene rings and of the consequent coplanarity of the two benzene rings in a substituted biphenyl of this sort (I):



(I) (II) (III)

In the second case there is again a possibility of conjugation of the electrons of the chlorine atom with the electron system of 2-nitrobiphenyl (p, π-conjugation) and of coplanarity in such a molecule (II). In this case we cannot exclude the possibility, also, of the presence in 2-chloro-2'-nitrobiphenyl of a certain "ortho effect", which manifests itself in the interaction between the electron cloud of the chlorine atom and the positive charge on the nitrogen atom of the nitro group (III).

EXPERIMENTAL

Experiments on the decomposition of aryldiazonium fluoborates were carried out in a four-necked flask fitted with mercury-sealed stirrer, thermometer, and reflux condenser. The fourth neck was used for the addition of the diazonium salt.

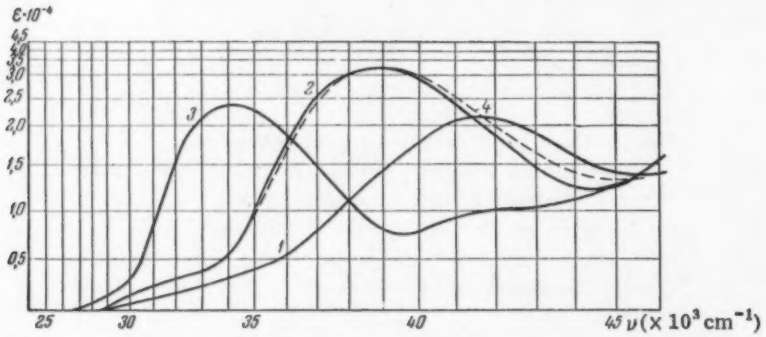


Fig. 6. Absorption curves of solutions in isooctane:
1) ethyl 2'-nitro-4-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 2) ethyl 3'-nitro-4-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 3) ethyl 4'-nitro-4-biphenylcarboxylate ($1 \cdot 10^{-4}$ mole/liter); 4) product of the decomposition of p-(ethyoxycarbonyl) benzenediazonium fluoborate in nitrobenzene (0.0271 g/liter).

Decomposition of Benzenediazonium Fluoborate in Nitrobenzene. In repeating the decomposition of benzenediazonium fluoborate in nitrobenzene [1] and in the decomposition of other aryldiazonium fluoborates, we added benzene to the reaction mixture (obtained by addition of the diazonium salt with stirring, further stirring, and cooling) before it was treated with sodium hydroxide solution; the tar was also washed carefully with hot benzene. The combined benzene solutions were then washed with 10% sodium hydroxide solution and with water, and were dried with calcium chloride; benzene was then distilled off, etc.

For the purpose of spectrographic analysis, the experiment was repeated under the above-described conditions, but in this and subsequent experiments, distillation of the reaction product (after removal of benzene and also of most of the nitrobenzene under somewhat reduced pressure) was carried out not under reduced pressure, but with superheated steam (temperature of oil bath 220-240°). The distillate was extracted with ether and the extract was dried with calcium chloride; ether was distilled off, and nitrobenzene was distilled off under reduced pressure; the residue was a red partially crystallized mass which, without further distillation, was subjected to spectrographic

examination together with standards, namely, the 3-nitrobiaryl (obtained in the main experiment) and the 2- and 4-nitrobiaryls.

4-Nitrobiphenyl was obtained a) by the decomposition of diazotized aniline in nitrobenzene in presence of sodium acetate; it was recrystallized from ethanol; m.p. 113-114° (the literature [10] gives 113-114°); b) by nitration of biphenyl with a mixture of nitric acid (sp. gr. 1.42) and glacial acetic acid; it was recrystallized from ethanol; m.p. 113-114°.

2-Nitrobiphenyl was prepared by the decomposition of diazotized o-nitroaniline in benzene in presence of sodium acetate by the Gomberg-Hey method; it was recrystallized from ethanol; m.p. 36.5-37.5° (the literature [11] gives 37°.

Decomposition of p-Toluenediazonium Fluoborate in Nitrobenzene. In the course of three hours 103 g (0.5 mole) of the diazonium salt was added to 250 g (2 moles) of nitrobenzene at 75°; the mixture was then kept at 80-85° for one hour. The mixture was treated as in the preceding experiment. After removal of benzene and nitrobenzene (under reduced pressure), the residue was vacuum-distilled. An oil (1.95 g) came over at 170-175° and 5 mm; it solidified. After crystallization from ethanol and from heptane it had m.p. 74.5-75.7° (m.p. of 4'-methyl-3-nitrobiphenyl 77.5° [12]).

Found %: C 73.25; 73.03; H 5.26; 5.22 $C_{13}H_{11}NO_2$. Calculated %: C 73.33; H 5.20

A solution of 0.8 g (1 molecular proportion) of the resulting methylnitrobiphenyl in 35 ml of glacial acetic acid was boiled with chromic acid mixture (1.67 g, i. e. 1.5 molecular proportions, of sodium dichromate, 1.2 ml of concentrated sulfuric acid, and 7.5 ml of water) for six hours. The precipitate formed on dilution with water was dried and crystallized from glacial acetic acid; m.p. 301° (m.p. of 3'-nitro-4-biphenylcarboxylic acid 301° [13]).

Found %: C 63.90; 64.11; H 3.97; 3.99 $C_{13}H_9O_4N$. Calculated %: C 64.20; H 3.73

4-Methyl-4'-nitrobiphenyl was prepared by Gomberg's method, together with 4'-methyl-2-nitrobiphenyl, by the decomposition of diazotized p-toluidine in nitrobenzene in presence of alkali; it was crystallized from alcohol and had m.p. 144° (m.p. of 4-methyl-4'-nitrobiphenyl 144° [13]). 4'-Methyl-2-nitrobiphenyl was obtained simultaneously with 4-methyl-4'-nitrobiphenyl (see above); it was isolated after the separation of 4-methyl-4'-nitrobiphenyl by distillation of the more readily fusible fractions and crystallization from alcohol; m.p. 37° (m.p. of 4'-methyl-2-nitrobiphenyl 37° [12]). It was identified further by reduction and acetylation to 2'-p-tolylacetanilide, m.p. 102-103° (the literature [7] gives 103°).

Decomposition of p-Anisolediazonium Fluoborate in Nitrobenzene. In the course of four hours 128 g (1 molecular proportion) of the diazonium salt was added to 300 g (4 molecular proportions) of nitrobenzene at 130°; the mixture was then kept at 135° for 90 minutes. The treatment was as in the preceding experiments. Fractionation gave: Fraction I, b.p. 73° (2-3 mm), nitrobenzene; Fraction II, b.p. 120-210° (3 mm), a reddish-yellow oil (3.75 g) which solidified in the condenser. Crystallization from heptane and alcohol gave colorless crystals, m.p. 82° (yield 2.86%).

Found %: C 68.34; 68.20; H 5.03; 5.11 $C_{13}H_{11}O_3N$. Calculated %: C 68.11; H 4.84

The methoxynitrobiphenyl so obtained (3 g) was heated in an oil bath (200-220°) with 9 g of pyridine hydrochloride for six hours. When the mixture was cool the precipitate was extracted with ether, and the ether extract was washed with dilute hydrochloric acid and with water; ether was distilled off. The semisolid residue was vacuum-distilled over heated zinc dust; the product was extracted with ether, the extract was washed with 10% sodium hydroxide solution and water, and ether was distilled off. The residue was crystallized from methanol. The melting point, alone and in admixture with 3-nitrobiphenyl, was 59°.

In this and subsequent experiments the spectrographic analysis of the semisolid mass obtained by distillation with superheated steam could be carried out only after the removal of a very small amount (2-3% by weight) of dark-colored tar, which was analyzed separately. The dark-colored semisolid mass was therefore freed from the tar by a single wash with well- cooled alcohol, and it was then submitted to spectrographic analysis.

4-Methoxy-4'-nitrobiphenyl was prepared by Jones and Chapman's method [14]: nitration of 4-biphenylyl benzoate, hydrolysis of the resulting 4'-nitro-biphenylylbenzoates, and methylation of the product [p-(p-nitrophenyl)phenol] with dimethyl sulfate. After crystallization from alcohol it had m.p. 111° (the literature [15]

gives 111° for 4-methoxy-4'-nitrobiphenyl). 4'-Methoxy-2-nitrobiphenyl was prepared by the decomposition of diazotized o-nitroaniline in anisole in presence of sodium acetate. A fraction of boiling point 142° (2 mm) was collected. After crystallization of carbon tetrachloride it had m.p. 64° (for 4'-methoxy-2-nitrobiphenyl the literature [14]gives m.p. 64°).

Qualitative examination of the absorption spectrum of the tar removed from the reaction product by alcohol treatment in this experiment (see above), and also in subsequent experiments, showed that these tars retain the general character of the spectrum of the m-isomer, but the first absorption band (in the region 25,000-35,000 cm^{-1}) is much more intense than that of the m-isomer. The alcoholic solution of the tar, therefore, contains the m-isomer, though in smaller amount than in the reaction product itself. The resinification products (tars) themselves did not give characteristic spectra.

Decomposition of p-Chlorobenzenediazonium Fluoborate in Nitrobenzene. The amounts taken were 130 g (1 molecular proportion) of p-chlorobenzenediazonium fluoborate and 300 g (4 molecular proportions) of nitrobenzene. Addition lasted for three hours at 120°, and the further treatment was for one hour at 125°. After the usual treatment and the removal of most of the nitrobenzene, vacuum distillation gave 2.56 g of a reddish oil, b.p. 95-120° (0.01 mm), which solidified when allowed to stand. After crystallization from methanol and light petroleum ether it had m.p. 89° (for 4'-chloro-3-nitrobiphenyl the literature gives m.p. 89° [16]). 4-Chloro-4'-nitrobiphenyl was isolated as a higher-melting substance by the decomposition of diazotized p-chloroaniline in nitrobenzene in presence of sodium acetate; after recrystallization from heptane it had m.p. 143° (for 4-chloro-4'-nitrobiphenyl the literature [17] gives m.p. 143°). 4'-Chloro-2-nitrobiphenyl was isolated in the decomposition of diazotized p-chloroaniline in nitrobenzene in presence of sodium acetate in the form of a fraction of b.p. 140-170° (4 mm). After crystallization from alcohol and from heptane it had m.p. 64° (for 4'-chloro-2-nitrobiphenyl the literature [18] gives m.p. 59-61°).

Decomposition of o-(Methoxycarbonyl)benzenediazonium Fluoborate in Nitrobenzene. In the course of two hours 126 g (0.5 mole) of the diazonium salt was added to 274 g (2.2 moles) of nitrobenzene at 120°. The mixture was then kept at 125° for one hour. A fraction of b.p. 110-225° (4 mm) isolated in the first distillation was refractionated at 4 mm:

Fraction I, b.p. 71°, nitrobenzene
Fraction II, b.p. 150-190°; 2.5 g
Fraction III, b.p. 190-200°; 2.7 g

Fraction II and III solidified. When fractionally crystallized from ethanol both of these fractions gave substances of m.p. 86-87°, undepressed by mixing them together.

Found %: C 65.47; 65.72; H 4.36; 4.33; N 5.83; 5.90 $C_{14}H_{11}O_4N$. Calculated %: C 65.37; H 4.31 N 5.44

The resulting methyl nitro-2-biphenylcarboxylate (0.4 g) was hydrolyzed by boiling it for three hours with 25 ml of 10% alcoholic potassium hydroxide. Removal of alcohol and acidification with hydrochloric acid gave an acid of m.p. 265° (from methanol).

Found %: C 61.45; 61.51; H 3.60; 3.65; $C_{13}H_9O_4N$. Calculated % C 61.66; H 3.58

A mixture of 10.5 g of o-iodotoluene, 12.4 g of 1-iodo-3-nitrobenzene, and 15 g of copper powder was heated at 270° for 30 minutes. In the vacuum fractionation of the product a fraction of b.p. 155-160° (4 mm) was collected. After crystallization from ethanol it had m.p. 68-71° (for 2-methyl-3'-nitrobiphenyl the literature [12] has 71°).

Oxidation of the crystals of m.p. 68-71° (0.9 g) with chromic acid mixture gave an acid of m.p. 260° (from ethanol). By saturation of a boiling methanol solution of this acid with hydrogen chloride we obtained the methyl ester of the acid. After crystallization from ethanol, its melting point, alone and in admixture with the methyl nitro-2-biphenylcarboxylate obtained by the decomposition of o-(methoxycarbonyl)benzenediazonium fluoborate in nitrobenzene, was 86-87°.

Found %: C 65.50; 65.70; H 4.35; 4.32 $C_{14}H_{11}O_4N$. Calculated %: C 65.37; H 4.31

Methyl 4'-nitro-2-biphenylcarboxylate was prepared by the decomposition of diazotized methyl anthranilate in nitrobenzene in presence of sodium acetate by isolation of the higher-boiling and higher-melting fraction

of b.p. 197-200° (4-5 mm). After crystallization from methanol it had m.p. 79-80° (for methyl 4'-nitro-2-biphenylcarboxylate the literature [19] gives m.p. 75-76°.

Found %: C 65.99; 66.12; H 4.30; 4.31 $C_{14}H_{11}O_4N$. Calculated %: C 65.37; H 4.31

Its melting point in admixture with the product of the decomposition of o-(methoxycarbonyl)benzenediazonium fluoborate in nitrobenzene (m.p. 86-87°) was 56-78°.

2-Methyl-2'-nitrobiphenyl was prepared by Sadler and Powell's method by the condensation of 1-iodo-2-nitrobenzene with o-iodotoluene in presence of copper. In the vacuum distillation it had b.p. 155-167° (5 mm), and after crystallization from alcohol it had m.p. 62° (for 2-methyl-2'-nitrobiphenyl Sadler and Powell [20] give m.p. 64°).

Oxidation of 2-methyl2'-nitrobiphenyl with chromic acid mixture gave an acid having m.p. 168° (from chloroform) (for 2'-nitro-2-biphenylcarboxylic acid the literature gives 168° [21] and 165-166.5° [20]). Boiling of this acid in absolute methanol with passage of hydrogen chloride gave methyl 2'-nitro-2-biphenylcarboxylate, m.p. 56-58° (from heptane).

Found %: C 65.30; 65.48; H 4.38; 4.51 $C_{14}H_{11}O_4N$. Calculated %: C 65.37; H 4.31

Decomposition of p-(Ethoxycarbonyl)benzenediazonium Fluoborate in Nitrobenzene. In the course of two hours 95 g (0.36 mole) of the diazonium salt was added to 204 g (1.7 moles) of nitrobenzene at 90°. The mixture was kept at 95° for one hour. After the usual treatment and removal of nitrobenzene under reduced pressure, the residue was vacuum-distilled. An oil (3.5 g) came over at 160-200° (3 mm) and rapidly solidified. After crystallization from ethanol it had m.p. 113-114.5° (for ethyl 3'-nitro-4-biphenylcarboxylate the literature [22] gives 113.7-114.4°).

Ethyl 4'-nitro-4-biphenylcarboxylate was prepared by the esterification of 4'-nitro-4-biphenylcarboxylic acid, m.p. 338° (Berliner and Blommers [22] give m.p. 336.2-339.2° for 4'-nitro-4-biphenylcarboxylic acid), in boiling ethanol with passage of hydrogen chloride, and the acid itself was prepared by the oxidation of 4-methyl-4'-nitrobiphenyl with chromic acid mixture. After crystallization from heptane the ester had m.p. 112° (the literature [22] gives m.p. 112.2-112.5° for ethyl 4'-nitro-4-biphenylcarboxylate).

Ethyl 2'-nitro-4-biphenylcarboxylate was prepared from 2-nitro-4'-methylbiphenyl, m.p. 37°, by its oxidation with chromic acid mixture to 2'-nitro-4-biphenylcarboxylic acid, m.p. 250° (from alcohol) (the literature [7] gives 250°), which was then esterified in boiling ethanol with passage of hydrogen chloride. After crystallization from heptane it had m.p. 71-72°.

Found %: C 66.27; 66.40; H 5.01; 4.97; $C_{15}H_{13}O_4N$. Calculated %: C 66.35; H 4.83

Decomposition of o-Chlorobenzenediazonium Fluoborate in Nitrobenzene. In the course of two hours 100 g (0.42 mole) of the diazonium salt was added to 230 g (1.9 moles) of nitrobenzene at 130°. The mixture was kept at 130° for one hour. The usual treatment was given. After the removal of nitrobenzene we obtained a fraction (12.2 g) of b.p. 185-193° (7-8 mm). After crystallization from methanol and heptane it had m.p. 71° (for 2-chloro-2'-nitrobiphenyl the literature [23] gives 71°). The substance showed no depression of melting point in admixture with 2-chloro-2'-nitrobiphenyl isolated from the products of the Gomberg decomposition of diazotized o-chloroaniline.

Decomposition of o-Nitrobenzenediazonium Fluoborate in Nitrobenzene. In the course of four hours 100 g (0.4 moles) of the diazonium salt was added to 225 g (1.8 moles) of nitrobenzene at 120°. This temperature was maintained until white fumes ceased to be evolved (a further four hours). A tar was deposited when the benzene solution was washed with 10 % sodium hydroxide solution; it was washed with benzene. The combined benzene solutions were washed with saturated NaCl solution and were dried with $CaCl_2$. Benzene and nitrobenzene (under somewhat reduced pressure) were distilled off, and the mixture was vacuum-distilled. A red viscous mass (15 g) came over at 165-210° (2 mm), and this partially crystallized out after a time. The crystals were filtered off from the red liquor, which did not crystallize after long standing; they amounted to 10 g; after two crystallizations from glacial acetic acid, m.p. 124°. The substance showed no depression of melting point in admixture with 2,2'-dinitrobiphenyl prepared from diazotized o-nitoaniline and cuprous chloride by Ullmann's method.

SUMMARY

1. In the decomposition of benzene-, p-toluene-, p-anisole-, p-chlorobenzene-, o-(methoxycarbonyl)benzene-, and p-(ethoxycarbonyl)benzene-diazonium fluoborates in nitrobenzene, the aryl group enters only the m-position in nitrobenzene. This is confirmed by analysis of the reaction products by the method of ultraviolet spectroscopy.

2. These reactions prove the heterolytic character of the decomposition of aryldiazonium fluoborates.

3. In the decomposition of o-nitro-and of o-chloro-benzenediazonium fluoborates in nitrobenzene only 2,2'-dinitro- and 2-chloro-2'-nitro-biphenyls, respectively, were isolated. An explanation is given for the causes of the formation of o-isomers in these two cases.

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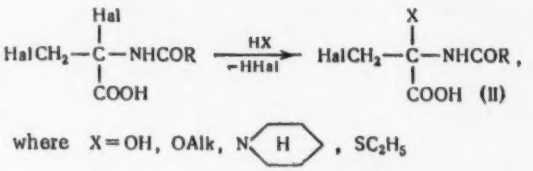
α,β-DISUBSTITUTED α-ACYLAMINO CARBOXYLIC ACIDS

COMMUNICATION 3. 2,2-BISACYLAMINO-3-HALOPROPIONIC ACIDS *

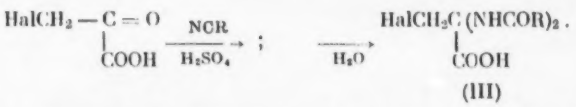
O. V. Kil'disheva, V. V. Shokina and I. L. Knunyants

It was shown previously that N-acyl-2,3-dihaloalanines (I) readily react with water, alcohols, amines, and thiols with formation of the corresponding 2-substituted-N-acyl-3-haloalanines (II) [1]. All attempts to prepare 2,2-bisacylamino-3-halopropionic acids (III) (X = NHCOR) by reaction of N-acyl-2,3-dihaloalanines with the corresponding amides were unsuccessful.



where X = OH, OAlk, N⟨H⟩, SC_2H_5

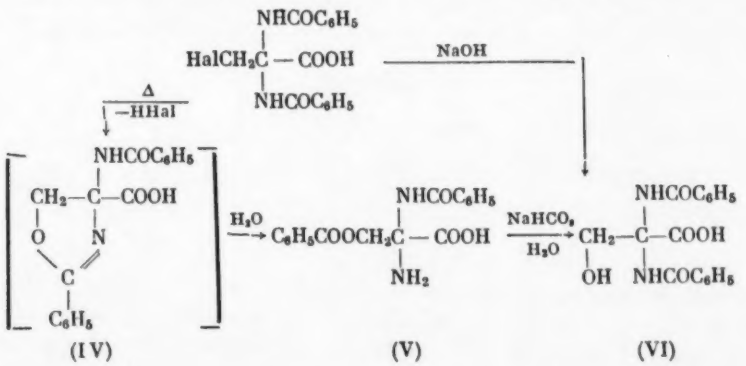
However, further investigation showed that 2,2-bisacylamino-3-halopropionic acids (III) are readily obtained by the condensation of halopyruvic acids with the corresponding nitriles in presence of concentrated sulfuric acid, which is similar to the known method of preparing α,α-bisacylamino carboxylic acids [2]:



(III)

In this way we prepared the 2,2-bisacylamino-3-halopropionic acids (III) listed in Table 1.

All the acids prepared were readily crystallized from the usual organic solvents, but they generally retained one solvent molecule. When 2,2-bisbenzamido-3-halopropionic acids were heated in alcohol or ethyl acetate, hydrogen halide was readily eliminated with formation of 4-benzamido-2-phenyl-2-oxazoline-4-carboxylic acid



(IV) (V) (VI)

* For Communication 2 see [1].

(IV), which under the action of water was hydrolyzed with formation of 2-amino-2-benzamido-3-(benzoyloxy) propionic acid (V), m.p. 148-150° (decomp.); the latter was insoluble in aqueous sodium bicarbonate. However, if the acid (V) was left for a long time in a saturated bicarbonate solution, migration of the benzoyl group from oxygen to nitrogen occurred with formation of 2,2-bisbenzamido-3-hydroxypropionic acid (VI), m p 162-163° (decomp), which was soluble in sodium bicarbonate solution. The mechanism of analogous reactions proceeding through the intermediate formation of oxazolinecarboxylic acids was studied thoroughly by Fry [3] for the case of N-benzoyl-3-chloroalanine.

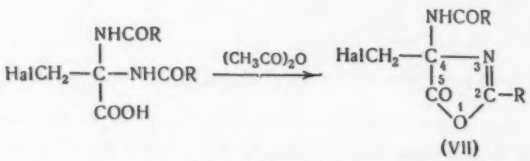
TABLE 1

$$HalCH_2—C(NHCOR)_2$$
$$|$$
$$COOH \cdot X$$

R	Hal	X solvent of crystallization	M.p. (°C)	Yield (%)	Found % / Calculated % C	H	Hal	N
C_6H_5	Cl	$CH_3COOC_2H_5$	161—162* (decomp.)	73	58,56 / 58,00	4,99 / 5,29	8,95 / 8,17	7,01 / 6,44
C_6H_5	Br	CH_3OH	157 (decomp.)	82	50,73 / 51,06	4,51 / 4,49	17,78 / 18,91	6,18 / 6,62
CH_3	Cl	H_2O	161—163	44	35,25 / 34,92	5,26 / 5,40	15,10 / 14,76	/ 11,64
CH_3	Br	H_2O	120	70	29,76 / 29,76	4,59 / 4,56	27,34 / 28,07	11,00 / 9,82

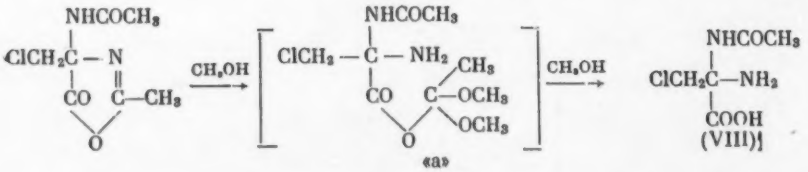
* A preparation of m.p. 140-141° which we described previously (obtained by the hydrolysis of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one [6] and of N-benzoyl-2,3-dichloroalanine [7]) was found, on further study, to be isomeric to the compound described in this communication, namely, 2,3-bisbenzamido-3-chloropropionic acid.

The dehydration of 2,2-bisacylamino-3-halopropionic acids by heating them with acetic anhydride led to the oxazolinones (VII) (Table 2).



(VII)

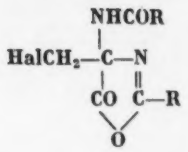
The oxazolinones obtained generally crystallized from the acetic anhydride in the form of stable colorless crystalline compounds. By the action of methanol on 4-acetamido-4-(chloromethyl)-2-methyl-2-oxazolin-5-one in absence of moisture we readily obtained 2-acetamido-2-amino-3-chloropropionic acid (VIII), m.p. 135°.



«a»

Such unusual cases of cleavage of the oxazole ring by alcohol with formation of the free amino acids instead of the esters have been met previously. Bergman and Grafe [4], and later, also, others [5], showed that some oxazolinones behave like imino esters and are readily converted by alcohols into ortho-esters of type "a", the

TABLE 2



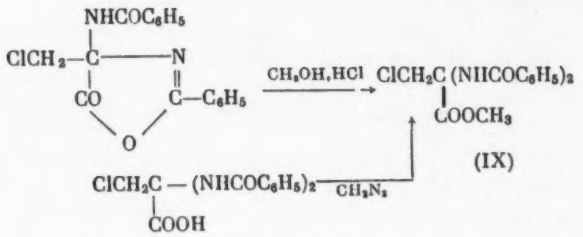
Hal	R	M.p. (°C)	Yield (%)	Found % / Calculated %			
				C	H	Hal	N
Cl	C_6H_5	190—191*	82	61,9 / 62,03	4,01 / 3,95	11,75 / 10,80	8,29 / 8,52
Br	C_6H_5	165—166**	80	54,14 / 54,69	3,63 / 3,48	22,10 / 21,4	7,21 / 7,21
Cl	CH_3	152	55***	39,43 / 41,07	4,37 / 4,4	17,80 / 17,3	
Cl	CH_3	135	55***	33,73	3,61	32,13	11,24

* Crystallized from alcohol.

** Crystallized from acetic anhydride.

*** Conditions of greater severity were necessary for the preparation of these oxazolinones: six times the amount of acetic anhydride and a temperature of 90-100° for 2-3 hours (until the acid was dissolved), after which the acetic anhydride was distilled off under reduced pressure, and the residue was washed with ether and recrystallized from acetic anhydride.

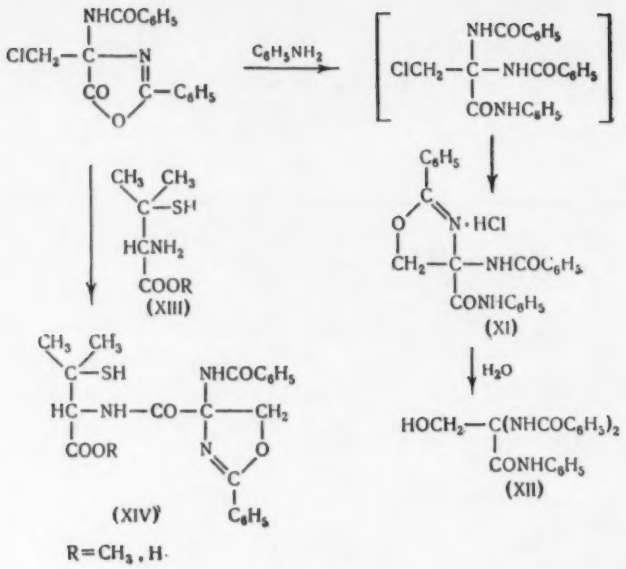
further hydrolysis of which leads to amino acids. However, 4-benzamido-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is not affected by alcohol, even at the boil, but in presence of a catalytic amount of HCl, the oxazolinone ring is opened in the usual way with formation of methyl 2,2-bisbenzamido-3-chloropropionate (IX), m.p. 174°,



(IX)

identical with the ester obtained by treating 2,2-bisbenzamido-3-chloropropionic acid with diazomethane. We must point out that in the treatment of 2,2-bisbenzamido-3-chloropropionic acid with ethereal diazomethane we obtained not only the ester (IX), but also some 4-benzamido-4-(chloromethyl)-2-phenyl-2-oxazoline-5-one.

Treatment of 2,2-bisacetamido-3-chloropropionic acid with diazomethane gave methyl 2,2-bisacetamido-3-chloropropionate (X), m.p. 164°. The reaction of 4-benzamido-4-(halomethly)-2-phenyl-2-oxazolin-5-ones with amines was generally accompanied by the elimination of hydrogen halide with formation of 2-oxazoline-4-carboxamides. Thus, in the reaction of equimolecular amounts of 4-benzamido-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one and aniline we isolated 4-benzamido-2-phenyl-2-oxazoline-4-carboxanilide hydrochloride (XI), m.p. 129-131°. When crystallized from aqueous alcohol this decomposed with formation of 2,2-bisbenzamido-3-hydroxypropionanilide (XII), m.p. 184-185°.



When equimolecular amounts of 3-mercaptovaline methyl ester (XIII, R = CH_3) and the oxazolinone (VII) (R = C_6H_5, Hal = Cl) were heated together, N-(4-benzamido-2-phenyl-2-oxazoline-4-carbonyl)-3-mercaptovaline methyl ester (XIV, R = CH_3), m.p. 147-148°, was isolated. Heating of 3-mercaptovaline with the same oxazolinone (VII) in presence of NaOH gave the compound (XIV, R = H), m.p. 147° (decomp.).•

EXPERIMENTAL

2,2-Bisacylamino-3-halopropionic Acids (III)

General Method of Preparation. The appropriate nitrile (0.04 mole) was added dropwise at a temperature of not above −5° to a stirred solution of 0.02 mole of the halopyruvic acid in ten times its volume of concentrated sulfuric acid. The reaction mixture was stirred for one hour under cooling and for three hours at room temperature, after which it was poured onto ice (ten times the volume of the sulfuric acid). The precipitate formed was filtered off, washed with water until neutral, and dried. It should be noted that bisacetamidochloropropionic acid was precipitated only after 1.5-2 hours. The acids usually crystallized with one molecule of solvent. The analytical data, melting points, and yields are given in Table 1.

2-Amino-2-benzamido-3-(benzoyloxy)propionic Acid (V)

A mixture of 1.17 g (0.003 mole) of 2,2-bisbenzamido-3-bromopropionic acid and 20 ml of methanol was boiled for 15 minutes, and 5-10 ml of cold water was then added. On the next day the crystalline precipitate was filtered off, washed with water and with alcohol, and dried in a vacuum over phosphorus pentoxide The product, which was obtained in 85.0% yield, was 2-amino-2-benzamido-3-(benzoyloxy) propionic acid, m.p. 150-152° (decomp.). This acid was not soluble in the usual organic solvents; it was insoluble in sodium bicarbonate solution.

Found %: C 62.18; H 4.84 $C_{17}H_{16}O_5N_2$. Calculated %: C 62.2; H 4.87

With diazomethane (V) gave its methyl ester, m.p. 138-140°, which readily gave its hydrochloride when treated with alcoholic HCl; the hydrochloride was reprecipitated from alcohol with ether and then melted with a little decomposition at 140°.

Found %: C 55.84; H 5.07; Cl 9.32; N 7.16 $C_{18}H_{19}O_5N_2Cl$. Calculated %: C 57.06; H 5.01; Cl 9.30; N 7.39

• See footnote in Experimental Part. — Publisher.

2,2-Bisbenzamido-3-hyroxypropionic Acid (VI)

2-Amino-2-benzamido-3-(benzoyloxy)propionic acid (0.5 g) was suspended in a saturated solution of sodium bicarbonate. After two hours an almost clear solution was obtained. On the next day the solution was acidified to Congo red with 2 N H_2SO_4; the oily precipitate formed gradually solidified. The precipitate was filtered off, washed with water, and dried in a vacuum over phosphorus pentoxide. The product, amounting to 0.35 g (70%), was 2,2-bisbenzamido-3-hydroxypropionic acid, m.p. 162-163° (decomp.).

Found %: C 62.02; H 4.85 $C_{17}H_{16}O_5N_2$. Calculated %: C 62.20; H 4.87

The acid (VI) can be repricipitated from sodium bicarbonate solution with acids and is readily soluble in alcohol and acetone.

4-(Acylamino)-2-alkyl(or aryl)-4-(halomethyl)-2-oxazolin-5-ones (VII)

General Method of Preparation. The 2,2-bisacylamino-3-halopropionic acid was mixed with four times its amount of acetic anhydride, and the mixture was heated at 80° for 3-5 minutes. One precipitate was rapidly replaced by another. The reaction mixture was cooled. The precipitate was filtered off and washed with ether. The oxazolinones were very soluble in alcohol and could be crystallized from acetic anhydride. Analytical data, melting points, and yield are given for these oxazolinones in Table 2.

2-Acetamido-2-amino-3-chlorporopionic Acid (VIII)

4-(Acetamido)-4-(Chloromethyl)-2-methyl-2-oxazolin-5-one (1 g) was dissolved in 6 ml of absolute methanol. After a few hours a crystalline precipitate began to form. The solution was left overnight in a refrigerator, and the precipitate was filtered off. The product, amounting to 0.75 g (85%), was 2-acetamido-2-amino-3-chloropropionic acid, m.p. 135°.

Found %: C 32.99; H 5.14; Cl 19.44 $C_5H_9O_3N_2Cl$. Calculated %: C 33.33; H 5.0; Cl 19.7

The acid (VIII) is readily soluble in water; it gives a positive reaction with ninhydrin only after the addition of a few drops of sodium bicarbonate solution.

Methyl 2,2-Bisbenzamido-3-chloropropionate (IX)

a) 2,2-Bisbenzamido-3-chloropropionic acid (0.5 g) was suspended in ether and treated with ethereal diazomethane. One precipitate was replaced by another. The precipitate was filtered off and repeatedly crystallized from absolute methanol. The product was methyl 2,2-bisbenzamido-3-chloropropionate, m.p. 172-174° (decomp.).

Found %: C 59.09; H 4.83; Cl 9.8; N 8.07 $C_{18}H_{17}O_4N_2Cl$. Calculated %: C 59.9; H 4.71; Cl 9.8; N 7.76

From the ethereal mother liquor we isolated 0.05 g of 4-benzamido-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one, m.p. 188-189° (from methanol). A mixture test with the oxazolinone obtained previously showed no depression of melting point.

b) 4-Benzamido-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.2 g) was heated with 2 ml of methanol containing 3% of dry HCl. Alcohol was removed, and the residue was crystallized from methanol. The product (0.1 g was methyl 2,2-bisbenzamido-3-chloropropionate, m.p. 168-169°, undepressed by admixture of the ester prepared by method (a).

Methyl 2,2-Bisacetamido-3-chloropropionate (X)

By the action of ethereal diazomethane on 2,2-bisacetamido-3-chloropropionic acid we obtained its methyl ester, m.p. 164°.

Found %: C 40.5; H 5.49; Cl 14.78 $C_8H_{13}O_4N_2Cl$. Calculated %: C 40.6; H 5.49; Cl 15.01

4-Benzamido-2-phenyl-2-oxazoline-4-carboxanilide Hydrochloride (XI)

Aniline (0.1 g, 0.001 mole) was added to a stirred suspension of 0.33 g (0.001 mole) of 4-benzamido-4-

(chloromethyl)-2-phenyl-2-oxazolin-5-one in 1 ml of dry ether. On the next day the reaction mixture was diluted with ether. The precipitate was filtered off and washed with dry ether. The product, which was obtained in quantitative yield, was 4-benzamido-2-phenyl-2-oxazoline-4-carboxanilide hydrochloride, m.p. 129-131°.

Found %: C 65.48; H 5.14; Cl 7.46; N 10.20 $C_{23}H_{20}O_3N_3Cl$. Calculated %: C 65.71; H 4.74 Cl 8.42; N 9.97

2,2-Bisbenzamido-3-hydroxypropionanalide (XII)

4-Benzamido-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one (0.37 g, 0.001 mole) was treated with aniline in the way described in the account of the previous experiment. The precipitate of 4-benzamido-2-phenyl-2-oxazoline-4-carboxanilide hydrobromide was dissolved in hot alcohol or acetone; the solution was cooled, and a few drops of cold water were added. The crystalline precipitate formed was filtered off. The product was 2,2-bisbenzamido-3-hydroxypropionanalide, m.p. 184-185°.

Found %: C 68.20; H 5.37; N 10.34 $C_{23}H_{21}O_4N_3$. Calculated %: 68.48; H 5.21; N 10.42

N-(4-Benzamido-2-phenyl-2-oxazoline-4-carbonyl)-3-mercaptovaline Methyl Ester (XIV, R = CH_3)

4-Benzamido-4-(Bromomethyl)-2-phenyl-2-oxazolin-5-one (0.37 g, 0.001 mole) was mixed with excess (0.4 g) of 3-mercaptovaline methyl ester, and the mixture was gradually heated to 80° over a period of five minutes; it was then cooled and extracted with dry ether. The ether extract was washed with 2 N H_2SO_4 and with water; it was then dried. Ether was removed, and the oily residue slowly solidified. We obtained 0.24 g of (XIV, R = CH_3), m.p. 146-147° with slight decomposition (from ether).

Found %: C 60.28; H 5.33; N 8.98 $C_{23}H_{25}O_5N_3S$. Calculated %: C 60.6; H 5.48; N 9.2

The ester (XIV, R=CH_3) decolorizes a solution of iodine in KI solution.

N-(2,2-Bisbenzamido-3-hydroxypropionyl)-3-mercaptovaline (XIV, R = H)*

A mixture of 0.37 g (0.001 mole) of 4-benzamido-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one, 0.15 g (0.001 mole) of 3-mercaptovaline, and 2 ml of 1 N NaOH (0.002 mole) was heated in a water bath for two hours. The resulting solution was filtered and acidified with 20% H_2SO_4. The precipitate formed was dissolved in saturated $NaHCO_3$ solution, and the solution was again acidified to Congo red with 2 N H_2SO_4. The product was (XIV, R=H), m.p. 147° (decomp.).

Found %: C 57.62; H 5.24; S 6.32; N 8.39 $C_{22}H_{24}O_6N_3S$. Calculated %: C 57.64; H 5.26; S 6.98; N 9.17

The compound (XIV) gives a positive reaction with $FeCl_3$ and decolorizes a solution of iodine in KI solution.

SUMMARY

1. Halopyruvic acids condense with nitriles with formation of 2,2-bisacylamino-3-halopropionic acids.

2. 2,2-Bisacylamino-3-halopropionic acids were converted into a) new serine derivatives containing a 2-(acylamino) substituent, and b) 4-(acylamino)-2-aryl(or alkyl)-4-(halomethyl)-2-oxazolin-5-ones.

3. The oxazolinones obtained were found to be powerful acylating agents. Acylation with these oxazolinones is generally associated with a secondary reaction in which the acylation product is converted into an (acylamino) oxazoline. By the hydrolysis of 4-acetamido-4-(chloromethyl)-2-methyl-2-oxazolin-5-one we obtained 2-acetamido-2-amino-3-chloropropionic acid, which is a new compound.

* The title and analytical data are given as in the original text. However, the substance named in the title is not (XIV, R=H), but the decylization product obtained by the addition of H_2O to (XIV, R=H). Its formula is $C_{22}H_{25}O_6N_3S$, not $C_{22}H_{24}O_6N_3S$. The formula of (XIV, R=H) would be $C_{22}H_{23}O_5N_3S$. — Publisher.

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DIRECT SYNTHESIS OF 1,1-DICHLOROSILYLCYCLOPENTANE

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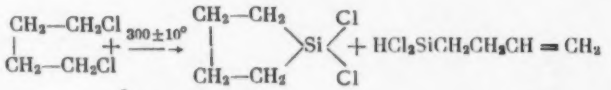
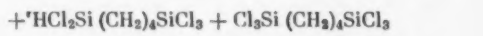
All known cyclic organosilicon compounds in which the ring is made up of carbon atoms and a silicon atom have been prepared previously only by the organometallic method of synthesis [1-4]. We recently reported [5] that the reactions of 3,4-dichloro-1-butene and of 1,4-dichloro-2-butene with copper-silicon alloy result in the formation of 1,1-dichlorosilacyclopent-3-ene.* It was of undoubted interest to study also the behavior of 1,4-dichlorobutane in the direct synthesis, because it would be expected that in this case also ring-closure would occur. Such behavior, however, would be contrary to the already existing data of English and co-workers [6], according to which the reaction of 1,4-dichlorobutane with silicon gives only 1,1,1,6,6,6-hexachloro-1,6-disilahexane in very low yield.

We were doubtful about these data, and we undertook an investigation in which we established the following: the main product of the reaction of 1,4-dichlorobutane with silicon is 1,1-dichlorosilacyclopentane (I). The yield of this compound (its content in the condensate) was 30%. Another monosilane, 3-butenyldichlorosilane (II), is evidently formed by the elimination of hydrogen chloride from 1,4-dichlorobutane and reaction of the product, 4-chloro-1-butene, with silicon. Proof of this was provided by our detection of 4-chloro-1-butene in the reaction mixture. Apart from these monosilanes, in the reaction of 1,4-dichlorobutane with silicon we isolated the disilicon compounds 1,1,1,6,6-pentachloro-1,6-disilahexane (III) and 1,1,1,6,6,6-hexachloro-1,6-disilahexane (IV). To confirm the correctness of the structures of the chlorosilanes they were converted into silahydrocarbons with the aid of methylmagnesium chloride, and these were then analyzed.

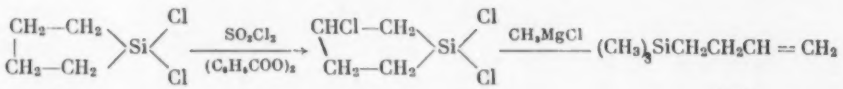


(I) (II)



(III) (IV)

We studied some chemical properties of 1,1-dichlorosilacyclopentane. Thus, in its chlorination with sulfuryl chloride, hydrogen on the β-carbon atom is replaced by chlorine. In the reaction of 1,1,3-trichlorosilacyclopentane (V) with methylmagnesium chloride, replacement of chlorine by methyl groups is accompanied by decyclization at the Si–C bond, or so-called β-decomposition [7]:



(I) (V) (VI)

The properties of the 3-butenyldichlorosilane (VI) formed by decyclization were found to be identical with those of the same substance as prepared by us previously by the Grignard-Wurtz reaction from trichloro(chloromethyl) silane and allyl bromide [8]. In the hydrolysis of 1,1-dichlorosilacyclopentane with aqueous alkali under the conditions used for the conversion of dichlorodiethylsilane into the corresponding diol [9] we isolated only a condensation product, a poly(tetramethylene siloxane). The reactions of 1,1-dichlorosilacyclopentane with allylmagnesium

* Prefix sila- = silyl or silico-, indicates presence of a single silicon atom.

bromide and with acetic anhydride went in the usual way, i. e. the chlorine atoms were replaced by allyl and acetoxy, respectively.

$$\underset{\text{VII}}{(CH_2)_4Si(CH_2CH=CH_2)_2} \xleftarrow{CH_2-CH-CH_2MgBr} \underset{\text{I}}{(CH_2)_4SiCl_2} \xrightarrow{(CH_3CO)_2O} \underset{\text{VIII}}{(CH_2)_4Si(OCOCH_3)_2}$$

Hydrogen bromide added vigorously to 1,1-diallylsilacyclopentane (VII) at −10°. The resulting dibromo compound $(CH_2)_4Si(CH_2CHBrCH_3)_2$ was unstable; when heated, it underwent β-decomposition with elimination of propene and formation of 1,1-dibromosilacyclopentane.

EXPERIMENTAL

Direct Synthesis. 1,4-Dichlorobutane (800 g) was passed at 23 g/hour through a tube filled with Si−Cu alloy at 300 ± 10°. Fractionation of 730 g of reaction mixture collected from the condenser gave: trichlorosilane, 38 g (5.3%); silicon tetrachoride, 44.5 g (6.1%); 4-chloro-1-butene, 24.3 g (3.3%), b.p. 74-75°, n'^{20}_D 1.4226 (the literature [10] gives b.p. 74.5-75.5°, n^{20}_D 1.4233) the Raman spectrum of this compound contained frequencies characteristic of the $CH=CH_2$ group; 3-butenyldichlorosilane (II), 36.5 g (5%), b.p. 125.5-127° (743 mm); n^{20}_D 1.4446, d^{20}_4 1.0724; 1,1-dichlorosilacyclopentane (I), 217 g (29.7%), b.p. 139.5° (732 mm); n^{20}_D 1.4645; d^{20}_4 1.1768; found MR* 36.40; calculated MR 36.67 (the literature [1,] gives m.p. 140-141° (752 mm), n^{20}_D 1.4644, d^{20}_4 1.1798; m.p. 141°, n^{20}_D 1.4651; d^{20}_4 1.1505); 1,1,1,6,6-pentachloro-1,6-disilahexane (III), 41 g (5.7%), b.p. 230° (729 mm); n^{20}_D 1.4792; d^{20}_4 1.3316; found MR 61.92, calculated MR 61.47.

Found %: C 17.52; H 3.09; Si 19.64 $C_4H_9Si_2Cl_5$. Calculated %: C 16.53; H 3.12; Si 19.33

1,1,1,6,6,6-hexachloro-1,6-disilahexane (IV), 44.5 g (6.1%), b.p. 251.5° (738 mm) m.p. 26.5-27°, n^{30}_D 1.4722; d^{30}_4 1.3823, found MR 65.86; calculated MR 65.47.

Found %: C 15.12; H 2.55; Si 18.00 $C_4H_8Si_2Cl_6$. Calculated %: C 14.78; H 2.48; Si 17.28

The residue amounted to 134 g (18.4%). In the calculation of yields the intermediate fractions were not taken into account. Increase in the rate of passage of 1,4-dichlorobutane from 23 to 30 g/hour reduced the yield of 1,1-dichlorosilacyclopentane from 29.7% to 25%.

Methylation of the Products of Direct Synthesis (IV)−(VII). The methylation was carried out with methylmagnesium chloride, which was taken in excess. The procedure was almost the same in all cases. Over a period of 40 minutes, 31 g (0.2 mole) of 1,1-dichlorosilacyclopentane was added to an ethereal solution of CH_3MgCl prepared from 14.6 g (0.6 mole) of magnesium and methyl chloride. The reaction mixture was heated in a water bath for seven hours, and was then treated with water and 5% hydrochloric acid. By distillation we isolated from the ethereal solution 12.6 g (55%) of 1,1-dimethylsilacyclopentane; b.p. 104.5° (73 mm); $n^{20}D$ 1.4340; d^{20}_4 0.7893.

Found %: C 63.30; H 12.22; Si 24.17 $C_6H_{14}Si$. Calculated C 63.97; H 12.35; Si 24.58

The literature [1, 2] gives b.p. 105° (742 mm); n^{20}_D 1.4348; d^{20}_4 0.7939; b.p. 107°, n^{25}_D 1.4335; d^{25}_4 0.780.

From (II) we obtained 3-butenyldimethylsilane, b.p. 98.5° (735 mm); n^{20}_D 1.4161; d^{20}_4 0.7292; found MR 39.33, calculated MR 39.33.

Found %: C 62.75; H 12.44; Si 24.51 $C_6H_{14}Si$; Calculated %: C 63.08; H 12.36; Si 24.56

From (III) we obtained 2,2,7-trimethyl-2,7-disilaoctane, b.p. 182° (752 mm); n^{20}_D 1.4341; d^{20}_4 0.7770; found MR 63.18; calculated MR 63.32.

Found %: C 56.87; H 12.36; Si 30.02 $C_9H_{24}Si_2$. Calculated %: C 57.35; H 12.84; Si 29.81

From (IV) we obtained 2,2,7,7-tetramethyl-2,7-disilaoctane, b.p. 191.7° (746 mm); n^{20}_D 1.4270; d^{20}_4 0.7652 (the literature [3] gives b.p. 199° (748mm); n^{25}_D 1.4244; d^{25}_4 0.763.

1,1-Diallylsilacyclopentane. Over a period of two hours 19.5 g (0.8 mole) of magnesium in ether suspension was added to a mixture consisting of 31 g (0.2 mole) of 1,1-dichlorosilacyclopentane and 72.6 g (0.6 mole) of allyl bromide. The reaction mixture was boiled for seven hours, part of the ether was distilled off, and heating was continued further for 90 minutes at 70-80°. In the usual way we isolated from the ethereal solution 16.7

* Molar refractivity.

g (50.3%) of 1,1-diallylsilacyclopentane, b.p. 196.2° (738 mm); n^{20}_D 1.4851; d^{20}_4 0.8581; found MR 55.56; calculated MR 55.35.

Found %: C 72.43; H 10.75; Si 16.70 $C_{10}H_{18}Si$. Calculated %: C 72.20; H 10.91; Si 16.89

Addition of HBr to 1,1-Diallylsilacyclopentane. At a temperature from −5° to −10°, 11.3 g of 1,1-diallylsilacyclopentane was saturated with hydrogen bromide until the theoretical increase in weight had occurred. Distillation of the reaction mixture gave the product of β-decomposition, 1,1-dibromosilacyclopentane, b.p. 178-180°; n^{20}_D 1.5240; d^{20}_4 1.7126.

Chlorination of 1,1-Dichlorosilacyclopentane. A mixture of 83 g (0.54 mole) of 1,1-dichlorosilacyclopentane, 73 g (0.54 mole) of sulfuryl chloride, and 1 g of benzoyl peroxide was heated until the evolution of gas had completely stopped (four hours). Fractionation gave 36.6 g of 1,1,3-trichlorosilacyclopentane b.p. 184.2° (752 mm), n^{20}_D 1.4879; d^{20}_4 1.3248; found MR 41.22; calculated MR 41.51.

Found %: C 25.46; H 3.62 $C_4H_7SiCl_3$ Calculated %: C 25.34; H 3.72

and 10 g of a substance of b.p. 210-215°, n^{20}_D 1.4929; d^{20}_4 1.4239; which was probably a dichloro derivative of 1, 1-dichlorosilacyclopentane; found MR 45.71; calculated MR 46.35.

Reaction of 1,1,3-Trichlorosilacyclopentane with CH_3MgCl. 1,1,3-Trichlorosilacyclopentane (34 g, 0.18 mole) was added to methylmagnesium chloride prepared from 13.13 g (0.54 mole) of magnesium and methyl chloride in either. The reaction mixture was heated for seven hours on a water bath; we isolated 5.8 g (25.2%) of 3-butenyltrimethylsilane, b.p. 110.5° (752 mm); n^{20}_D 1.4149; d^{20}_4 0.7372 (the literature [8] gives b.p. 111.5-112.5°; n^{20}_D 1.4148; d^{20}_4 0.7358). The Raman spectrum of the silahydrocarbon obtained was identical with that given in the literature [8].*

1,1-Diacetoxysilacyclopentane. A mixture of 23.4 g (0.15 mole) of 1,1-dichlorosilacyclopentane and 30.6 g (0.3 mole) of acetic anhydride was boiled for eight hours in a flask fitted with reflux condenser protected by a calcium chloride tube. Fractionation gave 22.3 g (73.5%) of 1,1-diacetoxysilacyclopentane, b.p. 92-93° (5 mm); n^{20}_D1.4408, d^{20}_4 1.1143; found MR 47.92; calculated MR 48.19.

Found %: C 47.38; H 6.84; Si 13.99 $C_8H_{14}SiO_4$. Calculated %: C 47.53; H 6.93; Si 13.86

Hydrolysis of 1,1-Dichlorosilacylopentane. In the treatment of 1,1-dichlorosilacyclopentane by the procedure given in [9] we succeeded in isolating only a polysiloxane having d^{20}_4 1.1285.

Found %: C 48.16; H 8.20; Si 27.26 $[C_4H_8SiO]_n$. Calculated %: C 47.94; H 8.05; Si 28.03

SUMMARY

1. The behavior of 1,4-dichlorobutane in direct synthesis was investigated. It was shown that the main reaction product is 1,1-dichlorosilacyclopentane.

2. The reaction of 1,1-dichlorosilacyclopentane with sulfuryl chloride, acetic anhydride, allylmagnesium bromide, and aqueous alkali were studied.

3. 1,1,3-Trichlorosilacyclopentane, which is formed in the chlorination of 1,1-dichlorosilacyclopentane, undergoes β-decomposition with opening of the ring when it reacts with a Grignard reagent.

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* Raman spectra were kindly determined by Iu. P. Egorov.

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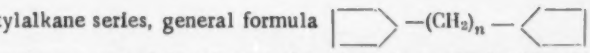
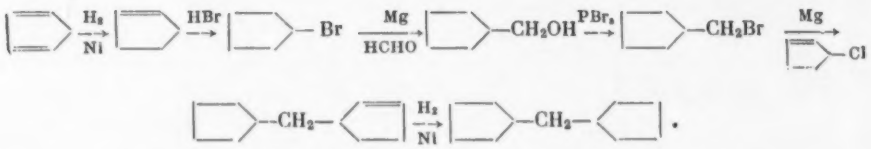
PREPARATION OF DICYCLOPENTYLMETHANE AND 1,3-DICYCLOPENTYLPROPANE FROM CYCLOPENTADIENE

A. F. Plate and V. I. Stanko

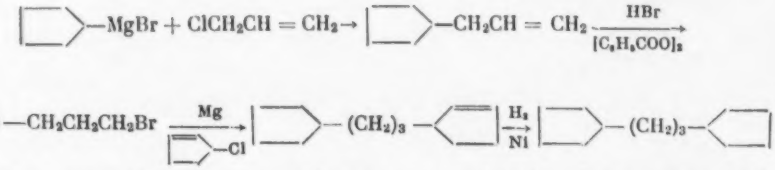
Hydrocarbons of the α,ω-dicyclopentylalkane series, general formula  have not yet been detected in petroleums, though analogous containing six-member rings, in particular bicyclohexyl and its homologs, have been found in petroleums. This is possibly to be explained by the fact that under the conditions of formation and migration of petroleum these structures change into other, more stable ones; thus it was shown, for example, that under the action of aluminum chloride bicyclopentyl is readily and quantitatively isomerized into decahydronapthalene [1]. However, it is possible that the absence of suitable standards has made it impossible to detect hydrocarbons of this series in petroleums. α,ω-Dicyclopentylalkanes have, in fact, received quite inadequate study and have scarcely been described in the literature until recently, whereas α,ω-dicyclohexylalkanes have been studied much more thoroughly. With the object of studying the physical properties and Raman spectra of these hydrocarbons we undertook the synthesis [2,3] of the first members of the α,ω-dicyclopentylalkane series, and, inclusive of the hydrocarbons whose synthesis is described in this paper, we have prepared hydrocarbons containing two five-membered rings and having the above general formula with values of n ranging from 0 to 5.

Dicyclopentylmethane was prepared previously by Nenitzescu and Cioranescu [4] in the following way. In the reaction of cyclopentanecarbonyl chloride with cyclopentene in presence of cyclohexane as solvent, addition of the acid chloride occurred at the double bond and this was followed by replacement of the chlorine atom by hydrogen from cyclohexane, which in this case served as a reducing agent. The resulting dicyclopentyl ketone was subjected to Clemmensen reduction. We considered that with this method of synthesis partial isomerization of the five-membered ring into a six-membered one is possible, and we therefore selected another method, in which the starting material was cyclopentadiene and in which ring isomerization was in our view impossible:



The constants of the dicyclopentylmethane obtained were, in fact, somewhat different from those cited in the literature.

The synthesis of the previously undescribed 1,3-dicyclopentylpropane was carried out as follows:



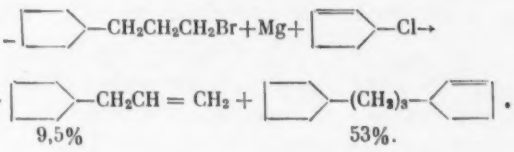
In the reaction of (3-bromopropyl) cyclopentane with magnesium and 3-chlorocyclopentene the formation of

TABLE 1

Physical Properties of α,ω-Dicyclopentylalkanes

Hydrocarbon	B.p. (°C at 10 mm)	n_D^{20}	d_4^{20}	Literature references
Bicyclopentyl	64,5—64,6	1,46429	0,8656	[5]
Dicyclopentylmethane	83,3—83,4	1,46777	0,8675	Present paper
1,2-Dicyclopentylethane	99,2—99,3	1,46628	0,8620	[2]
1,3-Dicyclopentylpropane	115,4	1,46658	0,8611	Present paper
1,4-Dicyclopentylbutane	130,3—130,4	1,46727	0,8606	[3]
1,5-Dicyclopentylpentane	143,2—143,3	1,46816	0,8604	[3]

1-(2-cyclopenten-1-yl)-3-cyclopentylpropane was accompanied by the formation also of allylcyclopentane; an analogous case has been found previously [3]. Reaction proceeds as follows:



The table gives the physical constants of the α,ω-dicyclopentylalkanes that we prepared.

EXPERIMENTAL

Cyclopentene was prepared by the partial hydrogenation of cyclopentadiene [6]. Bromocyclopentane was prepared by the addition of hydrogen bromide to cyclopentene.

Synthesis of Dicyclopentylmethane. A Grignard reagent was prepared from 298 g (2 moles of bromocyclopentane and 49 g (2.01 g-atom) of magnesium in 800 ml of dry ether, and by the action of gaseous formaldehyde on this we obtained 103 g (51.5%) of cyclopentanemethanol, which had b.p. 106-108°(82 mm) and 59-60° (20 mm); $n^{20}D$ 1.4575; d_4^{20} 0.9322 (the literature [7] gives b.p. 162-162.5°; $n^{20}D$ 1.4579; d_4^{20} p,9313).

Reaction of 86 g (0.86 mole) of cyclopentanemethanol with 86 g (0.32 mole) of phosphorus tribromide gave [7] 46 g (33%) of (bromomethyl)cyclopentane. The fraction collected had b.p. 58-62° (20 mm); $n^{20}D$ 1.4859; d_4^{20} 1.2920 [the literature [7] gives b.p. 56-57° (17 mm)].

2-Cyclopenten-1-ylcyclopentylmethane. A solution of 26 g (0.25 mole) of 3-chlorocyclopentene in 50 ml of dry ether was added under cooling (0-5°) to a Grignard reagent prepared from 46 g (0.28 mole) of (bromomethyl) cyclopentane and 7.5 g (0.31 g-atom) of magnesium in 250 ml of dry ether. The reaction mixture was stirred for one hour at room temperature and for one hour at the boiling point of the ethereal solution. After the usual treatment of the reaction mixture with water and dilute sulfuric acid, the ethereal solution was dried, ether was distilled off, and the reaction product was distilled from a column of 45-plate efficiency having a copper filling. We isolated 5 g of bi-2-cyclopenten-1-yl and 16 g (42% on the amount of 3-chlorocyclopentene) of 2-cyclopenten-1-ylcyclopentylmethane with the following constants, b.p. 80.5-80.7° (11 mm); $n^{20}D$ 1.4778; d^{20}_4 0.8813; found MR 48.16; calculated for $C_{11}H_{18}F$ MR48.13. 2-Cyclopenten-1-ylcyclopentylmethane (16 g) was hydrogenated in the cold in acetone (50 ml) solution over Raney nickel in an autoclave at a pressure of 75-80 atm. The resulting dicyclopentylmethane was washed free from acetone and dried; it was purified chromatographically on 20 g of silica gel. and 14 g of the product was then fractionated through a column of 45-plate efficiency; for further purification of hydrocarbon was again passed through 15 g of silica gel.

The dicyclopentylmethane had the following properties: b.p. 83.3-83.4° (10 mm); $n^{20}D$ 1.46777; d^{20}_4 0.8675; found MR 48.60; calculated for $C_{11}H_{20}$ MR48.60 (the literature [4] gives b.p. 208-210°; $n^{20}D$ 1.46974; d^{20}_4 0.8710). The rather high constants of Nenitzescu and Cioranescu are probably to be explained by the presence of an isomer with a six-membered ring as impurity.

Found %: C 86.94; 87.07; H 13.20; 13.10 $C_{11}H_{20}$. Calculated %: C 86.84 H 13.16

Synthesis of 1,2-Dicyclopenthylpropane. Allylcyclopentane (56 g, yield 51%) was prepared from 24.3 g (1 g-atom) of magnesium, 149 g (1 mole) of bromocyclopentane, and 76.5 g (1 mole of allylchloride. The allylcyclopentane had the following properties: b.p. 125.8-126.1° (751 mm) $n^{20}D$ 1.4409; d^{20}_4 0.7931 (the literature [8] gives b.p. 125.8-126.5° (737 mm); $n^{20}D$ 1.4408; d^{20}_4 0.7939).

(3-Bromopropyl)cyclopentane. A rapid stream of hydrogen bromide was passed for four hours through a solution of 5 g (0.03 mole) of benzoyl peroxide in 56 g (0.51 mole) of allylcyclopentane contained in a three-necked flask fitted with tube for the passage of gas, reflux condenser, and thermometer, and the temperature of the reaction mixture was maintained at 20-30° by cooling the flask. The reaction mixture was washed with sodium carbonate solution and with water and was dried with calcium chloride, after which it was vacuum-distilled. We recovered 12 g of unchanged allylcyclopentane and isolated 66 g (86% of the allylcyclopentane that reacted) of a mixture of bromo compounds, b.p 109-116° (37 mm). In order to separate the bromo compounds, the mixture was vacuum-fractionated through a 15-plate column with a glass filling, and we obtained 16 g (20.9%) of (2-bromopropyl)cyclopentane and 46 g (60.3%) of (3-bromopropyl)cyclopentane. The (2-bromopropyl)cyclopentane had b.p. 99.5° (30 mm); $n^{20}D$ 1.4818; d^{20}_4 1.2126; found MR 44.88; calculated for $C_8H_{15}Br$, MR 44.71; and the (3-bromopropyl)cyclopentane had b.p. 108.5° (30 mm), $n^{20}D$ 1.4842; d^{20}_4 1.2227; found MR 44.70 calculated for $C_8H_{15}Br$, MR 44.71.

When in addition of hydrogen bromide to allylcyclopentane is carried out in absence of benzoyl peroxide at a temperature of from −25° to −30°, then (2-bromopropyl)cyclopentane having the above constants is obtained in 61% yield [5].

1-(2-Cyclopenten-1-yl)-3-cyclopentylpropane. A solution of 21 g (0.21 mole) of 3-chlorocyclopentene in 100 ml of dry ether was added with cooling at a temperature of from 0° to −5° to the Grignard reagent prepared from 42 g (0.22 mole) of (3-bromopropyl)cyclopentane and 5.3 g (0.22 g-atom) of magnesium in 200 ml of dry ether. The mixture was stirred for 30 minutes at room temperature and for 30 minutes at the boiling point of the ethereal solution. On the next day the reaction mixture was decomposed by water and dilute hydrochloric acid. Ether was distilled off, and by fractionation of the reaction product we isolated two fractions: Fraction I (6 g), b.p. 30-45° (24 mm), and Fraction II (29 g), b.p. 130-145° (24 mm). Fractionation of Fraction I through a column of 45-plate efficiency gave 2.3 g (10%) of allylcyclopentane, b.p. 126.2° (763 mm); $n^{20}D$ 1.4409; d^{20}_4 0.7928 (see above for data in literature). Vacuum fractionation of Fraction II through the same column gave 21 g (53%) of 1-(2-cyclopenten-1-yl)-3-cyclopentylpropane, which had the following constants: b.p. 113.1° (9 mm); $n^{20}D$ 1.4754; d^{20}_4 0.8774; found MR 57.20; calculated for $C_{13}H_{22}F$ MR 57.36.

1-(2-Cyclopenten-1-yl)-3-cyclopentylpropone (21 g) was hydrogenated in acetone (25 ml) solution over 5 g of Raney nickel in an autoclave in the cold at a pressure of 74-80 atm. The hydrocarbon was washed free from acetone and then subjected to chromatographic purification on 20 g of silica gel. We obtained 19.5 g of 1,3-dicyclopentylpropane, which was distilled through the 45-plate column and again passed over 15 g of silica gel. 1,3-Dicyclopentylpropane had the following properties: b.p. 115.4° (10 mm); $n^{20}D$ 1.46658; d^{20}_4 0.8611; found MR 57.96; calculated for $C_{13}H_{24}$, MR 57.83.

Found %: C 86.67; 86.59; H 13.43; 13.37; $C_{13}H_{24}$. Calculated %: C 86.67; H 13.33

SUMMARY

1. A new method of synthesizing dicyclopentylmethane is described. The starting material is cyclopentadiene.

2. The following previously undescribed hydrocarbons containing two five-membered rings were prepared: 1,3-dicyclopentylpropane, 2-cyclopenten-1-ylcyclopentylmethane, and 1-(2-cyclopenten-1-yl)-3-cyclopentylpropane.

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CATALYTIC TRANSFORMATIONS OF m-XYLENE IN PRESENCE OF ALUMINUM SILICATES

N. I. Shuikin, E. D. Tulupova and Z. P. Poliakova

The study of the conditions required in the catalytic isomerization of m-xylene is receiving much attention by both foreign and Russian workers. This problem arises from the necessity of expanding the resources of p-xylene which is the starting material for the manufacture of a synthetic fiber.

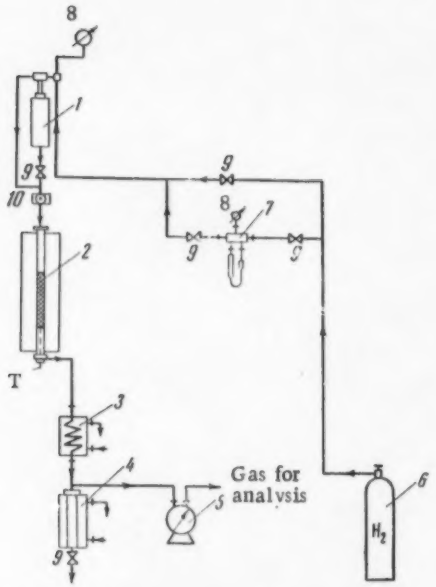
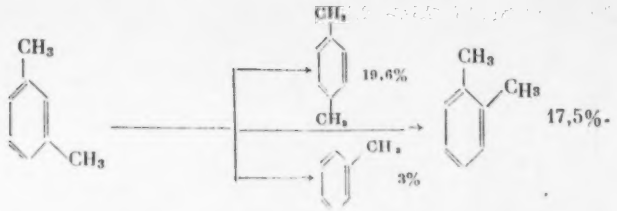


Fig. 1. Flow apparatus for experiments carried out under pressure (Type II):
1) dropper; 2) reactor; 3) condenser; 4) receiver; 5) gas meter; 6) cylinder of H_2; 7) flowmeter; 8) manometer; 9) valve; 10) inspection glass; T = thermocouple.

In 1954-56 papers appeared on the isomerization of m-xylene in presence of a synthetic aluminum silicate catalyst [1-3]. Boedeker and Erner [1] investigated the vapor-phase isomerization of a technical mixture of xylene at 515° and atmospheric pressure and obtained catalyzates that were enriched to an extent of 11.6% in p-xylene. It was shown also that doubling the space velocity (change from 0.6 to 1.2 hour^{-1}) has no substantial effect on the yield of p-xylene, whereas reduction in pressure reduces the tendency for the occurrence of side reactions. Sulimov and co-workers [2] subjected a technical mixture of C_8 aromatic hydrocarbons containing 4-6% of p-xylene, and also pure m-xylene, to an isomerization treatment, and they found that at 500° and atmospheric pressure, the content of p-xylene in the catalyzate was close to its equilibrium value. Mamedaliev, Topchiev, and others [3] carried out the isomerization of m-xylene under reduced pressure (50 mm) at 450° and obtained an isomerizate containing 21.8% of the p-isomer. Pitts and Connor [4] showed that, in presence of a platinized aluminum silicate at 482° and under a pressure of hydrogen of 12.5 atm., m-xylene is isomerized with formation of p-xylene in a yield of 82.3% of the equilibrium amount. There are also some patents [5] and a review article [6] on the problem of obtaining p-xylene.

The object of the present investigation was to determine the conditions required in the isomerization of m-xylene in presence of gumbrin*(from the Georgian SSR), of a synthetic aluminum silicate catalyst obtained from Ufa oil refinery, and also of alumina at various temperatures and pressures. We investigated also the same catalysts containing deposits of small amounts (0.5-1%) of finely dispersed platinum. On the basis of data in the literature and the experimental material reported in this paper, we may conclude that the most suitable and accessible catalysts for the isomerization of m-xylene into p-xylene are aluminum silicates (natural and synthetic). Of the catalysts that we investigated, the most effective was activated gumbrin, in presence of which at 450° and atmospheric pressure and at a space velocity of 0.5 hour^{-1}, the transformation of m-xylene follows the following scheme:

* Fuller's earth. - Publisher.



EXPERIMENTAL

The isomerization experiments were carried out with pure m-xylene obtained from the Khar'kov Tar Distillery; it had b.p. 137° (740 mm); $n^{20}D$ 1.4973; d^{20}_4 0.8642.

Alumina was prepared by treating of 1 M aluminium nitrate with 12% ammonia solution at room temperature. The precipitate of aluminum hydroxide was washed with distilled water until NO_3^- ions were removed completely. Gumbrin was first treated at the boil with 20% hydrochloric acid for four hours, after which it was washed with distilled water until a test for chloride ions was negative. * After this treatment the precipitates were dried at 100° and then formed into cylinders 4 mm in height and 4 mm in diameter. Gumbrin and the synthetic aluminum silicate catalyst were roasted at 500° in a muffle. The platinum-containing catalysts were prepared by impregnation of the carrier with dilute chloroplatinic acid solution at room temperature; this was followed by drying at 110° and reduction with electrolytic hydrogen at 300°.

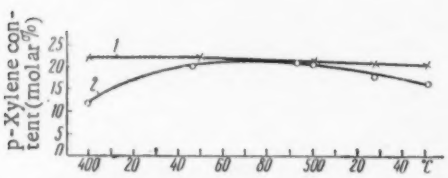


Fig. 2. Temperature-dependence of the p-xylene content of the catalyzate (gumbrin as catalyst):
1) calculated values; 2) experimental values.

Experiments at atmospheric and reduced pressures were carried out in the usual laboratory flow apparatus, and those carried out under a pressure of hydrogen were carried out in a simplified flow apparatus, which is shown diagrammatically in Fig. 1. The reactor 2 is a seamless steel tube of internal diameter 22 mm contained in an aluminum bronze block heated by an electric furnace. The temperature was measured with a thermocouple contained in a pocket in the reactor, and it was maintained at the required level within ± 3° by means of an electronic regulator. The m-xylene was placed in a steel cylinder (the dropper 1). The rate of feed of the xylene was controlled by valve. The required amount of hydrogen was fed into the reactor through the special flowmeter 7, which was graduated for the pressure of hydrogen used in the experiment. The catalysis products passed to the coil condenser 3 and further to the separator-receiver 4 in which liquid and gaseous reaction products were separated. The gaseous products were passed through the gas meter 5 either to a gas holder for analysis or into the atmosphere. In all cases the reactor contained 100 ml of catalyst. The space velocity of the feed of m-xylene was 0.5 $hour^{-1}$. Each experiment was carried out with 50 g of m-xylene.

The liquid isomerization products were fractionated through a column of 35-plate efficiency. The refractive indexes and densities of the fractions were determined. The hydrocarbon compositions of the xylene fractions were established with the aid of Raman spectra** and by the method of nitration with subsequent determination of the m-isomer in the form of its trinitro derivative, which was crystallized from acetone [7]. p-Xylene was determined after the crystallization of its 2,3- and 2,6-dinitro derivatives from ethanol. The amount of o-isomer was determined by difference. The gas formed was analyzed in an Orsat-Lunge apparatus. The gas obtained in experiments with gumbrin at 500° and atmospheric pressure consisted entirely of methane. In experiments

* After a treatment with hydrochloric acid the gumbrin had the following composition: SiO_2—86.98%, Al_2O_3—4.14%, —Fe_2O_3 0.56%, MgO—1.27%, CaO—1.33%, TiO_2—0.41%. H_2O—1.66%. The ignition losses amounted to 5.54%.

** The Raman spectra were investigated by Iu. P. Egorov and I. P. Iakovlev, to whom the authors express their thanks.

TABLE 1

Characteristics of Isomerizates Obtained from m-Xylene in Presence of Aluminum Silicate Catalysts

Expt.	Catalyst	Temp. in °C (p in atm)	Yield of liquid catalyzate (%)	Fractional and individual compositions of catalyzate (%)											Losses
				up to 108°	108—112°	112—135°	135—140°			140—145° mainly o-xylene	145—154°	154—160°	160—165°	165—170°	
							o-xylene	p-xylene	m-xylene						
1	Synthetic	500 (1)	94,0	1,0	11,4	2,6	8,0	15,0	33,5	12,5	1,6	0,8	7,2	5,0	1,4
2	Gumbrin	400 (1)	98,8	—	—	2,2	7,0	12,3	67,0	9,0	—	—	—	—	2,5
3	The same portion	450 (1)	98,0	—	3,0	0,4	11,1	19,6	58,3	6,4	—	—	—	—	1,2
4	Gumbrin (fresh)	500 (1)	97,5	0,6	4,7	1,7	5,6	20,0	53,3	8,5	0,6	0,7	2,5	—	1,8
5	The same portion	500 (1)	98,0	0,5	5,0	1,5	7,7	15,0	58,9	9,6	—	—	—	—	1,8
6	The same portion after regeneration	500 (1)	97,5	0,2	3,8	2,0	10,9	17,8	50,0	6,5	1,6	2,7	3,7	—	0,8
7	The same portion after regeneration	527 (1)	97,3	0,2	5,0	1,5	6,1	18,6	52,0	5,7	1,8	2,1	3,5	1,2	2,3
8	The same portion after regeneration	550 (1)	94,2	0,3	9,1	1,1	11,7	17,3	46,1	2,6	1,5	1,2	6,0	1,1	2,0
9	Gumbrin (fresh)	400 (15)	98,5	0,5	1,3	1,0	9,6	12,0	64,5	9,5	—	—	—	—	1,6
10	The same portion	450 (15)	98,0	0,3	2,0	0,8	8,2	13,0	60,0	8,2	1,4	1,4	2,3	—	2,4
11	The same portion	500 (15)	97,5	0,5	4,5	1,3	9,0	13,2	60,1	2,8	1,4	1,3	2,3	1,5	2,2
12	Gumbrin (fresh)	450(50 *mm*)	99,5	—	—	0,3	7,1	15,6	64,6	9,8	—	—	—	—	2,6
13	0.5% Pt-gumbrin	500 (1)	97,3	—	5,9	0,9	9,4	12,9	56,7	5,5	1,7	1,2	4,0	—	1,8
14	0.5% Pt-gumbrin	500 (15)	97,5	0,3	8,6	1,8	11,0	15,0	42,4	6,9	0,5	1,2	2,9	7,0	2,4
15	1% Pt-synthetic aluminum silicate	400 (1)	98,0	0,7	4,7	2,1	7,0	14,3	50,0	10,0	2,0	1,6	3,0	2,5	2,1
16	1% Pt-synthetic aluminum silicate	450 (1)	97,5	0,8	9,0	0,9	8,3	16,4	49,2	2,1	0,9	1,4	4,0	4,8	2,4
17	1% Pt-synthetic aluminum silicate (fresh portion)	500 (1)	95,0	1,7	12,4	2,0	6,3	18,8	38,0	6,5	1,2	1,0	6,0	4,9	1,2

TABLE 2

Transformation of m-Xylene in Presence of Al_2O_3 and of 1% Pt–Al_2O_3

Experiment	Catalyst	Temp. of expt. (°C)	Pressure (atm)	Yield of liquid catalyzate (%)	Composition of catalyst (%)*				
					toluene	o-xylene	p-xylene	m-xylene	trimethylbenzenes
1	Al_2O_3	500	(1)	98,0	—	—	3,0	97,0	—
2	Al_2O_3	500	(15)	96,6	—	—	5,0	95,0	—
3	1%Pt–Al_2O_3	500	(1)	94,0	5,5	8,9	13,2	65,7	2,5
4	1%Pt–Al_2O_3	500	(15)	94,0	4,7	9,3	11,6	63,4	5,5

* No account has been taken in this table of the head (up to 108°) and intermediate fractions, which in various experiments ranged from 1% to 5%.

at 500° in presence of hydrogen under pressure, the out-going gas consisted of hydrogen (90.6%) and methane (9.4%). The characteristics of the catalyzates and their compositions are given in Tables 1 and 2. The variation with temperature of the p-xylene contents of isomerizates obtained in the catalytic treatment of m-xylene with gumbrin is shown in Fig. 2.

The results given in Table 1 show that, of the catalysts investigated, the most active for the isomerization of m-xylene is gumbrin. The optimum reaction conditions are: 450°, atmospheric pressure, space velocity of the feed of m-xylene 0.5 $hour^{-1}$. The Raman spectrum indicated the presence of 19.6% of p-xylene in the catalyzate obtained under these conditions (Experiment 3, Table 1). As a by-product we isolated 3.0% of toluene. The catalyzate came over in the range 108-145°. Its yield was 98.0%. At 500°, with other conditions unchanged, the yield of p-xylene attained 97.1% of the equilibrium concentration. However, at this temperature the yields of by-products were higher: from the catalyzate we isolated 4.7% of toluene and 2.5% of mesitylene (see Experiment 4, Table 1). The material balance at 500° was as follows:

Liquid catalyzate 97.5%
Coke 1.2%
Gas 0.3%
Losses 1.0%

Curve 2, Fig. 2, shows that at 450-500° the p-xylene content of the isomerizate attains almost the equilibrium value [8]. Further rise in temperature leads to reduction in the yields of p-xylene at the expense of increased formation of by-products.

The results obtained at reduced pressure (50 mm) at 450° (Experiment 12, Table 1) are worthy of serious attention. In this case we obtained almost 100% of liquid catalyzate, and this contained 15.6% of p-xylene.

The gumbrin catalyst can be regenerated by air at 500°, after which its isomerizing power is almost completely restored (Experiments 6-8, Table 1). The use of hydrogen under pressure favored the formation of toluene and C_9 aromatic hydrocarbons (Experiments 9-11,14, Table 1). The synthetic aluminum silicate was found to be a less selective catalyst than gumbrin. Under similar reaction conditions it was more favorable to the formation of by-products (Experiments 1 and 15-17, Table 1), and it also increased the amount of gas formed.

The results of Experiments 13-17 (Table 1) showed that the introduction of platinum into the aluminum silicate catalysts did not contribute to the smoothness of the isomerization reaction, so that no advantage was gained by its use. The characteristics of the catalyzates obtained from m-xylene in presence of Al_2O_3 and 1% Pt–Al_2O_3 are given in Table 2.

The results of the experiments listed in Table 2 show that in presence of Al_2O_3, m-xylene undergoes very little isomerization with formation of 3-5% of p-xylene. Introduction of 1% of platinum into the Al_2O_3 increases the extent of the transformation of m-xylene to a substantial degree. In this case, apart from m- and p-xylenes,

4.7-5.5% of toluene, up to 9.3% of o-xylene, and 2.5-5.5% of trimethylbenzenes were found in the catalyzates. However, under the given conditions the yield of p-xylene did not exceed 66.0% of the equilibrium concentration. From the data in Table 2 it can be seen that platinized alumina is a less suitable catalyst for the isomerization of m-xylene than gumbrin.

SUMMARY

1. A study was made of the conditions required for the isomerization of m-xylene in presence of gumbrin and of a synthetic aluminum silicate catalyst at different temperatures and pressures.

2. In presence of gumbrin the isomerization of m-xylene proceeds most smoothly at 450° under atmospheric pressure and at a space velocity of 0.5 hour^{-1}. Under these conditions the yield of p-xylene attains 91.2% of the equilibrium amount.

3. The use of reduced pressure (50 mm) favors the complete elimination of undesirable methylation and demethylation reactions and makes it possible to obtain almost 100% of liquid catalyzate containing 15.6% of p-xylene. The use of hydrogen under pressure (15 atm) results in the complication of the isomerization reaction by side reactions.

4. The synthetic aluminum silicate was a less effective catalyst than gumbrin in that it favored side reactions and gas formation to a greater extent.

5. In presence of $Pt-Al_2O_3$ at 500°, m-xylene was again isomerized into the o- and p-isomers, but simultaneous formation of toluene (up to 5.5%) and trimethylbenzenes (up to 2.5%) occurred.

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PECULIAR FEATURES OF THE POLYMERIZATION OF STYRENE IN PRESENCE OF BIVALENT INITIATORS

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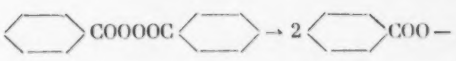
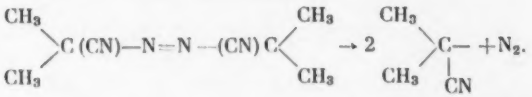
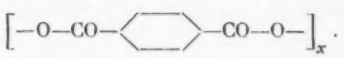
It is generally ackowledged that the nature of the initiator has an enormous effect on the polymerization process and to a certain extent determines both the conditions required for reaction and the properties of the polymer formed. This explains why so many investigations have been carried out in this direction [1]. However, all of these many investigations have been concerned with polymerization in presence of initiators that give univalent radicals in their decomposition. Well known examples of such initiators are benzoyl peroxide, 2,2'-azobis [2-methylpropionitrile], and cumene peroxide, which are broken down by heat with formation of univalent radicals, e. g.





The use of initiators that break down with formation of bi- and multi-valent radicals is still in the first stages of development, and there are only isolated papers in the literature on this matter. We may mention papers by Shah, Leonard, and Tobolsci [2] and Smets and Woodward [3], who used phthaloyl peroxide, by Waltcher [4], who used polymethyl methacrylate peroxide, and by Breitenbach and Kastel [5], who used pyrazolinetricarboxylic esters.

With the object of study the peculiar featres of polymerization in presence of bivalent initiators we investigated the polymerization of styrene in presence of phthaloyl and terephthaloyl peroxides. These peroxides were prepared from the corresponding acid chlorides and sodium peroxide [6] and were obtained as white powders, insoluble in the usual organic solvents and liable to explode when subjected to heat or shock. It is usually considered that these peroxides have polymeric structures [2]. The structure of terephthaloyl peroxide is probably to be represented as follows:



The structures of the radicals formed from these peroxides can therefore be represented both in monomeric (I) and polymeric (II) forms:

(I)

(II)

The results obtained in the polymerization of styrene in presence of these initiators (Tables 1 and 2) show that terephthaloyl and phthaloyl peroxides initiate the polymerization of styrene, but the reaction rate is much

TABLE 1

No.	Time (hours)	Initiator • benzoyl peroxide: yield of polymer (%)	η_{sp} ••	molecular wt.	terephthaloyl peroxide: yield of polymer (%)	η_{sp}	molecular wt.	phthaloyl peroxide: phthaloyl peroxide	η_{sp}	molecular wt.
1	1	20	0,15	17000	0,66	0,71	82000	2,44	0,86	99500
2	3	51	0,15	17000	1,39	1,05	121000	4,27	0,96	111000
3	6	97	0,16	18,00	3,12	1,36	157000	6,64	1,16	134000
4	12	100	0,19	22000	9,49	1,32	153500	11,59	1,23	142000
5	24	100	0,17	19600	14,25	1,91	222000	16,11	1,39	161000

• In all experiments the amount of initiator was 0.25 mole per cent; the polymerization temperature was 80°;

•• The viscosity was determined on a 0.5% solution in benzene.

lower than in the case of polymerization initiated by benzoyl peroxide, because of the very low solubilities of these initiators in styrene. Examination of the results shows that polymerization in presence of terephthaloyl and phthaloyl peroxides differs from that occurring in presence of benzoyl peroxide in that there is a regular continuous rise in the molecular weight of the polymer during the whole of the period of polymerization, with the result that polymers of much higher molecular weight are obtained.

TABLE 2

No.	Time (hours)	Initiator • benzoyl peroxide: yield of polymer (%)	η_{sp}	molecular wt.	terephthaloyl peroxide: yield of polymer (%)	η_{sp}	molecular wt.	phthaloyl peroxide: yield of polymer (%)	η_{sp}	molecular wt.
1	6	100	0,20	23100	11,60	0,81	93600	5,03	0,83	95900
2	12	100	0,17	19600	28,00	1,04	124700	18,20	1,01	116700
3	24	100	0,20	23100	61,00	1,55	179000	45,20	1,24	143200

• The polymerization temperature was 100°.

This peculiarity of polymerization in presence of bivalent initiators is probably to be explained as follows. The main cause of chain termination in free-radical polymerization is recombination, i.e. the combination of two growing macromolecules at their active ends. In the case of polymerization initiated by benzoyl peroxide, recombination results in the termination of the chain, i.e. in the formation of a macromolecule that is incapable of further growth:

$$C_6H_5COO-\left[-CH(C_6H_5)CH_2-\right]_x- + -\left[CH_2-(C_6H_5)CH-\right]_x-OOCC_6H_5 \longrightarrow$$

$$\longrightarrow C_6H_5COO-\left[CH(C_6H_5)CH_2\right]_{2x}OOCC_6H_5 .$$

The analogous reaction in the case of a bivalent initiator does not result in chain termination, because the recombination product, like the original macromolecules, remains an active molecule, having free valences at both ends of the chain and therefore continuing to grow in both directions. As a result the recombination does not hinder chain growth, which occurs throughout the whole of the period of polymerization with formation of

polymers of very high molecular weight. As relatively few univalent radicals are formed at the expense of the end groups of polymeric peroxides, their formation does not have much effect on the general polymerization picture.

TABLE 3

Decomposition temp. (°C)	Duration of decomposition (hours)	Amount of decomposed peroxide (%)
80	1	0.6
	2	3.9
	3	5.16
100	2	12.28
	3	24.8
	4	33.83
120	1	35.38
	2	43.87
	3	60.63
	4	73.96

EXPERIMENTAL

Terephthaloyl peroxide was prepared by treating a benzene or ether solution of the acid chloride with aqueous sodium peroxide. Terephthaloyl chloride was prepared by the method described for phthaloyl chloride [7]. For the preparation of the peroxide, a 10% aqueous sodium carbonate solution was cooled to 0°, and sodium peroxide (an equimolecular amount + 5% excess) was added; a cooled solution of the acid chloride was then added to the cooled mixture with vigorous cooling.* Stirring was continued for 15-20 minutes. The white amorphous precipate formed was filtered off and carefully washed with water, alcohol, and finally ether. The peroxide, dried at room temperature, was insoluble in the usual solvents; it exploded when struck and when heated to 130-135°.

As a result a very poor solubility of the peroxide obtained, the method of determining active oxygen used for its determination in soluble peroxides, e. g. acetyl and benzoyl peroxides, was not suitable. The most reproducible results were obtained by the following method: to a weighed amount (0.2-0.3 g) of the peroxide we added 30-40 ml of distilled water, 3 ml of 0.1 N NaOH, and an excess of potassium iodide solution. The mixture was kept for 3-4 hours at room temperature with periodic shaking. In the course of this time the sample of peroxide almost went into solution. Addition was made of 10 ml of 10% acetic acid, and after ten minutes the iodine liberated was titrated with 0.1 N thiosulfate. The peroxide obtained in the way described contained 80-90% of the theoretical amount of active oxygen; halogen was absent.

When heated at 80° or higher the peroxide lost active oxygen. To determine the extent to which decomposition occurs we took a peroxide sample containing 59.85% of the peroxide. The heating was carried out in ampoules. The results are given in Table 3.

The polymerization of styrene was carried out in sealed ampoules in an atmosphere of nitrogen. The styrene was first washed with dilute alkali and with water, dried over calcium chloride, and vacuum-distilled in the atmosphere of nitrogen; b.p. 32-34° (10 mm); $n^{20}D$ 1.5445. The amount of initiator used in the polymerization was 0.41 g per mole of styrene (0.25 mole per cent). After the polymerization reaction the contents of the ampoule were rapidly cooled and dissolved in benzene; the polymer was precipitated with methanol (the completeness of the precipitation was determined from the cessation of turbidity formation on addition of further amounts of methanol). The precipitated polymer was filtered off and dried at 100° to constant weight.

* In the preparation of terephthaloyl chloride with the aid of an ethereal solution of the acid chloride much care must be taken. The freshly prepared peroxide explodes when touched lightly.

SUMMARY

1. Data were obtained on the effect of the nature of the initiator on the course of the polymerization of styrene.

2. In presence of bivalent initiators the polymerization of styrene proceeds more slowly than in presence of univalent initiators, and it is accompanied by continuous rise in molecular weight through the polymerization process. The resulting polymers have higher molecular weights than those obtained with univalent radicals.

3. An explanation is proposed for the observed facts.

4. Polymeric terephthaloyl peroxide was synthesized.

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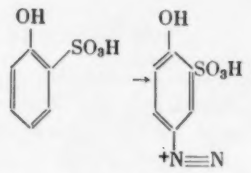
BRIEF COMMUNICATIONS

"DIAZOATION" OF p-HYDROXYBENZOIC AND 1-PHENOL-4-SULFONIC ACIDS*

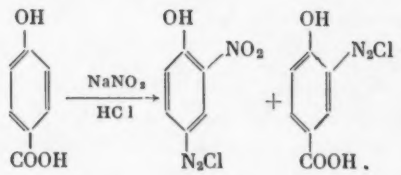
V. M. Belikov **

Rodionov and Matveev [1] showed that treatment of 1-phenol-2-sulfonic acid with an aqueous solution of nitrous acid results in the formation of a 4-hydroxy-3-sulfobenzenediazonium salt:



This reaction may be of great interest in the manufacture of intermediate products and dyes because it provides a new source of diazo compounds, namely phenols. However, the field of application of this reaction, which was investigated in detail by Nesmeianov and co-workers [2] for nonaqueous solutions of phenols, has scarcely been investigated at all for the aqueous solutions that are most commonly used in industry. Apart from the paper of Rodionov and Matveev already cited, there is only the communication by Nemodruk [3], who successfully applied the reaction to salicylic acid and 3-hydroxy-2-naphthoic acid, which gave 3-carboxy-4-hydroxybenzenediazonium and 2,3-dicarboxy-1-naphthalenediazonium salts, respectively.

We investigated the behavior of p-hydroxybenzoic acid, 1-phenol-4-sulfonic acid, p-hydroxybenzenediazonium salt, and Neville and Winther's acid toward an aqueous solution of nitrous acid. When a suspension of p-hydroxybenzoic acid in aqueous $NaNO_2$ was acidified, a diazo compound was obtained in 80-90% yield. Its structure was determined by Sandmeyer reaction with Cu_2Cl_2. In this reaction we isolated 4-chloro-2-nitrophenol and 3-chloro-4-hydroxybenzoic acid. The formation of these compounds enables us to suggest the following scheme for the diazoation of p-hydrobenzoic acid:



The replacement of the carboxy group of p-hydrobenzoic acid by nitroso under the action of nitrous acid was observed by Kostanecki [4]. The formation of 4-hydroxy-3-nitrobenzenediazonium chloride in our case may therefore be explained by the m-nitration of p-hydroxybenzoic acid, replacement of the carboxy group by nitroso, and conversion of nitroso into the diazo group by the mechanism proposed by Nesmeianov.

* The term "diazotization" is used in the Russian text with an explanatory footnote; we consider that the term "diazoation" is more appropriate for the reaction under discussion. – Publisher.

** This work was carried out under the direction and with the participation of Academician V. M. Rodionov.

5-Carboxy-2-hydroxybenzenediazonium chloride was formed by the normal Rodionov-Matveev reaction. The course of the diazoation reaction depends on the character and amount of the acid used for the acidification. Thus when excess of hydrochloric acid is used the yield of diazo compound is lowered to 40%, probably because of the reduction in the solubility of p-hydroxybenzoic acid in the reaction mixture. When acetic acid is used, much resinous material is formed; after the Sandmeyer reaction chloronitrophenol is obtained in 31% yield, but no chlorohydroxybenzoic acid is formed. A diazo compound is formed also in the action of nitrous acid on the solution of 1-phenol-4-sulfonic acid prepared by the decomposition of diazotized sulfanilic acid, but the structure of this diazo compound was not investigated. p-Hydroxybenzenediazonium salts and Neville and Winther's acid do not undergo the Rodionov-Matveev reaction.

Examination of the Rodionov-Matveev reaction on the basis of the mechanism proposed by Nesmeianov and the over-all process of the decomposition of HNO_2 in water shows that for completion of the reaction 4 moles of HNO_2 are required per mole of phenol.

The quantitative determination of the diazo compounds obtained was carried out by coupling then with methyl(sulfophenyl) pyrazolone, the excess of which was back-titrated with $NaNO_2$ solution, or by titration with 2-naphthol solution.

EXPERIMENTAL

Diazoation of p-Hydroxybenzoic Acid. Sodium nitrite (5.52 g, 0.08 mole) was added gradually to a suspension of 2.76 g (0.02 mole) of p-hydroxybenzoic acid in 100 ml of water at 15°; a smell of oxides of nitrogen appeared and the medium became acid to litmus. The reaction mixture was then gradually acidified with 7 ml of 36% hydrochloric acid. Stirring was continued, and after 1-2 hours the precipitate of p-hydroxybenzoic acid disappeared and the solution became homogeneous. The yield of diazo compound was 80-90%.

Sandmeyer Reaction. A solution of cuprous chloride in 10% hydrochloric acid was added to the solution of diazo compound. There was an immediate precipitate of the complex salt. The mixture was then heated under reflux in water bath for 3-4 hours; liberation of nitrogen occurred, the solution became clear, and a dark-colored oil separated. The reaction mixture was then treated in two ways. 1) It was extracted with ether, the ether extract was washed with 10% KOH solution, and the alkaline extract was acidified with hydrochloric acid and steam-distilled. Yellow crystals of 4-chloro-2-nitrophenol came over; m.p. 85-86° (the literature [5] gives 86-87°). 2) The chloronitrophenol was immediately steam-distilled from the reaction mixture. There remained a light-green solution, on which floated some brown resin. The resin was separated, and the solution was made alkaline; it was evaporated down to one-third bulk on a water bath, copper oxide was filtered off, and the filtrate was acidified and cooled. There was a precipitate of colorless crystals of 3-chloro-4-hydroxybenzoic acid, which melted, after sublimation, at 165-167° (the literature [6] gives 165-166°).

When cooled with snow the brown resin became crystalline and could be recrystallized from alcohol. Two substances were obtained; they had the character of azo compounds. One of them a red substance, had m.p. 136-140° (Decomp.), and the other, a brown substance, had m.p. 120-126° (decomp). Both substances contained chlorine, were insoluble in sodium carbonate solution, but were soluble in sodium hydroxide solution.

Preparation of a Solution of 1-Phenol-4-sulfonic Acid. Concentrated sulfuric acid (20 ml) was added to a solution of 39 g (0.2 mole) of technical sodium sulfanilate in 400 ml of water, and diazotization was effected at 20-25° with 13.8 g (0.2 mole) of 100% $NaNO_2$. When the diazotization was complete, 60 ml of concentrated sulfuric acid was added, and the mixture was heated at 90° until the diazo compound was completely decomposed, which was indicated by the cessation of the evolution of nitrogen and by the absence of a reddish color in a test with resorcinol on filter paper.

Diazoation of 1-Phenol-4-sulfonic Acid. A solution of 140 g of $NaNO_2$ in 180 ml of water was added very slowly with stirring to the solution of 1-phenol-4-sulfonic acid; the solution was introduced at a point below the level of the liquid. The yield of diazo compound was 75-89%; the total volume of solution was 950 ml.

SUMMARY

1. The Rodionov-Matveev reaction was extended to p-hydroxybenzoic acid and 1-phenol-4-sulfonic acid, and diazo compounds were obtained in yields of 75-90%.

2. When the Sandmeyer reaction was carried out on the diazo solution obtained from p-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid and 4-chloro-2-nitrophenol were formed. This indicates that the primary reaction products were 5-carboxy-2-hydroxybenzenediazonium and 4-hydroxy-3-nitrobenzenediazonium salts.

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HEAT OF HYDRATION OF 2-NITROPYRROLE

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In an investigation of the ultraviolet spectra of nitropyrroles we found that the positions of the absorption maxima differ in aqueous and nonaqueous solutions and depend on the amount of water present in the solvent [1]. The shift in the maximum can attain 30 mμ. This effect was ascribed to the hydration of solute molecules.

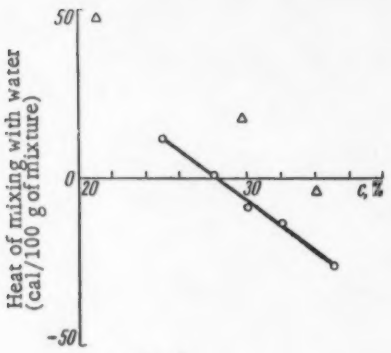

Fig. 1

In the present investigation, the hydration of 2-nitropyrrole was proved directly by measurement of the heat of hydration. For this purpose we used the following method. In order to exclude the heat of wetting and of breakdown of the crystal lattice, the substance was first dissolved in glacial acetic acid. It was shown in special experiments that the ultraviolet spectrum of 2-nitropyrrole in acetic acid is identical with its spectra in benzene and alcohol, which in our opinion indicates absence of solvation in these solvents. We then made use of the known fact [2] that the heat of dilution of acetic acid with water falls as the amount of acid increases, passes through zero, and then becomes negative: we diluted the acetic acid solution of the substance with water in such a way that the heat of mixing of the acetic acid itself with water would be zero. The absence of any thermal effect in the mixing of acetic acid with water was carefully checked in special experiments. Hence, the observed absorption of heat (1.7 kcal/mole) in the dilution of the 2-nitropyrrole solution must be ascribed entirely to hydration of the solute. In order to prove that this value is indeed the heat of hydration and does not include other thermal effects, we measured the heat of solution of 2-nitropyrrole in 28% acetic acid and in glacial acetic acid. As would be expected, the difference between these quantities was close to the value given above for the heat of hydration. We therefore consider that the observed change in the spectrum of 2-nitropyrrole is to be explained by its chemical interaction with water.

TABLE 1

CH_3COOH concn. in final soln. (%)	Amount of water (g)	Spec. heat capac. of the solution *	Δt (°C)	Thermal effect calc. per 100 g of solution (cal)
35	29,1	0,842	—0,245	—26
32	33,3	0,857	—0,133	—13,3
30	36,6	0,867	—0,074	— 8,2
28	40,3	0,877	+0,010	+ 1,0
25	47,0	0,892	+0,108	+11,8

*Interpolated from data in [4]. The heat capacity of the system was calculated from these data and the constant of the apparatus.

In the determination of the heats of mixing of acetic acid with water we found lack of agreement between our results and those of Sandonini [2] (triangles in Fig. 1). As our measurements show, the heat of mixing of acetic acids and water is zero when the acetic acid content of the final mixture is 28%. This lack of agreement is probably to be attributed to the difference in temperature: Sandonini worked at 16-18°, and we at 21-22°.

EXPERIMENTAL

The calorimeter used consisted of a Dewar vessel having a capacity of about 150 ml and provided with stirrer driven by a synchronous motor and a glass rod for crushing the ampoules. The temperature was read on a Beckmann thermometer with the aid of a lens. The ampoules consisted of thin-walled paraffin bottles, about 17 ml in volume [3]. The Dewar vessel was wound with three layers of asbestos string and had a cover of "organic glass". After each measurement the heat capacity of the system containing the investigated solution was determined by means of a stabilized alternating current or a direct current. For this purpose a current of 0.2-0.3 amp was passed for a certain time through a spiral of nichrome wire, diameter 0.1 mm, wound on the glass rod used for crushing the ampoules.

In the dilution experiments, the calculated amount of water was poured into the Dewar vessel, the paraffin ampoule filled with the liquid to be added was introduced into the water, and the apparatus left until the temperature was uniform (about 30 minutes). The ampoule was then crushed into small pieces, and the temperature was measured every 15 seconds accurately within 0.001°. The value of Δt was found graphically from the extrapolated values of temperature.

In the determination of the heat of mixing of acetic acid and water, in all experiments the amount of acetic acid (m.p. 16.4°, assaying at 100%) introduced into the ampoule was 15.68 g, and the required amount of distilled water was introduced into the calorimeter. The results of the experiment are given in the table and in the figure (circles).

For control purposes, the heat of neutralization (15 ml of 0.1 N HCl in the ampoule and 15 ml of 0.1 N NaOH + 20 ml of water in the calorimeter) was measured. A value of 13.2 kcal/mole was found.

In the measurement of the heat of hydration of 2-nitropyrrole a weighed amount (about 1 g) was dissolved in 15.68 g of acetic acid in the ampoule, and 40.3 g of water was introduced int the Dewar vessel. Change in temperature after mixing were −0.264° and −0.274° for samples of 1.0135 g and 1.1076 g, respectively. The direct determination of the heat capacity of this system gave the value 59.6 cal/degree, from which it is found that the thermal effects due to hydration were −15.72 and −16.32 cal., which when calculated per mole became −1.74 and −1.65 kcal/mole, respectively.

In the determination of the heat of hydration by the other method, heats of solution of 2-nitropyrrole in glacial and in 28% acetic acid were found in the following way. Glacial acetic acid (55 ml) was placed in the Dewar vessel, and a paraffin dish containing 0.9009 g of 2-nitropyrrole was placed on its surface. The dish was upset, and the temperature fell by 0.634°, which for a heat capacity of the system of 38.7 corresponds to a heat of solution of 3.0 kcal/mole. The dissolution of 2-nitropyrrole in the resulting solution (weight 0.5428 g, heat capacity 39.3, Δt = 0.362°) was accompanied by the same thermal effect. This indicates that there is no appreciable change in the structure of liquid acetic acid when 2-nitropyrrole is dissolved in it. The heat of solution in 28% acetic acid was measured similarly (weights of samples 0.3471 g and 0.8083 g, heat capacities 59.6 and 60.8, Δt 0.236° and 0.526°, respectively) and the values obtained were 4.6 and 4.4 kcal/mole. The difference between the heats of solution in 28% and in glacial acetic acid was −1.5 kcal/mole, which is close to the value given above for the heat of hydration of 2-nitropyrrole.

SUMMARY

1. The shift in the ultraviolet absorption maximum of 2-nitropyrrole resulting from change in solvent from glacial acetic acid to dilute acetic acid is associated with hydration of the solute molecules; the heat of hydration has a value of from −1.5 to −1.7 kcal/mole.

2. In the course of the investigation measurements were made on the heat of mixing of acetic acid and water at 21-22° for final concentrations of 25-35%. The heat of mixing is zero when the acetic acid content of the final mixture is 28%.

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VINYL COMPOUNDS OF HEAVY METALS

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In a series of previous communications two of us, and also Freidlina and co-workers, have described the syntheses and investigated the properties of a series of organometallic compounds in which the metal is attached to an olefinic carbon. These investigations were concerned mainly with the stereochemistry of metal substitutions and the quasicomplex properties of some of these substances; they covered 2-chlorovinyl [1], propenyl [2], isopropenyl [3], styryl [4], and other [5, 6] compounds containing unsaturated organic residues of organometallic substances of more complicated structure. In the course of the work we investigated numerous properties of these compounds which distinguished them from saturated organometallic compounds. We accumulated some material also on organometallic compounds containing the simplest of these groups, namely vinyl; until recently these have been unknown in the literature. As the syntheses of some vinyl organometallic compounds have been published recently [7-10], we now report on the vinyl compounds of heavy metals which we have synthesized.

By the action of vinylmagnesium bromide on mercuric bromide in tetrahydrofuran solution we obtained vinylmercury bromide, m.p. 169.5-171°, in 64% yield (the literature [9] gives m.p. 168-170°). The substance is readily symmetrized with sodium stannite with formation of liquid divinylmercury, which has an extremely unpleasant smell. When treated with 3% hydrochloric acid in the cold, this readily loses one vinyl group with formation of vinylmercury chloride.

From divinylmercury we obtained various other organometallic vinyl compounds by means of exchange reactions. Reaction of divinylmercury with mercuric chloride in tetrahydrofuran gave vinylmercury chloride, m.p. 183°, and its reaction with mercuric acetate in glacial acetic acid gave vinylmercury acetate, m.p. 90-91° (decomp.).

Found %: C 17.06; 17.09; H 2.31; 2.25 $C_4H_6O_2Hg$. Calculated %: C 16.76; H 2.11

Reaction of divinylmercury with lithium in ether and carbonation of the product gave acrylic acid, which was characterized in the form of 2,3-dibromopropionic acid. Reaction of divinylmercury with thallium trichloride gave divinylthallium chloride. This substance and divinylthallium bromide were prepared also by the action of thallium trichloride and tribromide, respectively, on vinylmagnesium chloride and bromide in a tetrahydrofuran-ether medium. These divinylthallium compounds are crystalline substances, which can be crystallized from pyridine and decompose, without melting, at about 300°.

When divinylthallium bromide is warmed with mercury in tetrahydrofuran, reaction proceeds as in the analogous case of diphenylthallium bromide; the product was divinylmercury, which was characterized in the form of vinylmercury bromide, m.p. 168.5°. Heating an aqueous solution of equivalent amounts of divinylthallium bromide and thallium tribromide gave vinylthallium dibromide, which, after crystallization from water, decomposed at 152-155°.

Found %: C 6.17; 6.05; H 0.66; 0.60 $C_2H_3TlBr_2$. Calculated %: C 6.14; H 0.77

Similarly, from the products of reaction between divinylthallium chloride and thallium trichloride, we isolated vinylthallium dichloride, which, after crystallization from water, decomposed at about 170°.

Found %: Cl 23.21; 23.27 $C_2H_3TlCl_2$. Calculated %: Cl 23.46

Exchange reactions between divinylthallium chloride or bromide and mercury, stannous chloride, and thallium halides gave vinyl derivatives of these metals:

$$(CH_2{=}CH)_2TlX \xrightarrow[X = Cl,\ Br]{\begin{array}{l} \xrightarrow{Hg} (CH_2{=}CH)_2Hg + TlX \\ \xrightarrow{SnX_2} (CH_2{=}CH)_2SnX_2 + TlX \\ \xrightarrow{TlX_3} 2CH_2{=}CHTlX_2 \end{array}}$$

By reaction of divinylthallium bromide with stannous bromide in acetone, we obtained divinyltin dibromide, b.p. 47° (2 mm); $n^{20}D$ 1.5920; d 2.1924; found MR 51.31; calculated MR 51.47.

Found %: C 14.62; 14.85; H 1.95; 1.85 $C_8H_4SnBr_2$. Calculated %: C 14.44; H 1.81

Similarly, from divinylthallium chloride and stannous chloride we obtained divinyltin dichloride, b.p. 53-55° (2 mm); $n^{20}D$ 1.5500; d^{20}_4 1.7621 (the literature [10] gives b.p. 54-56° (3 mm)).

EXPERIMENTAL

Divinylmercury. A solution of sodium stannite prepared from 4.02 g (0.017 mole) of $SnCl_2 \cdot 2H_2O$ in 36 ml of water and 8.27 g of NaOH dissolved in 36 ml of water was added to a solution of 10 g (0.0326 mole) of vinylmercury bromide in 120 ml of acetone. After 30 minutes a fraction of b.p. 58-87° was distilled from the reaction mixture; to this fraction saturated brine was then added. An oily product separated. The product from three experiments was collected and dried; it distilled at 90-91° (80 mm) and had $n^{20}D$ 1.5978; d^{20}_4 2.7713, found MR 31.34 calculated MR 30.55.* The yield was 53%.

Found %: C 18.90; 18.95; H 2.36; 2.41 C_4H_6Hg. Calculated %: C 18.86; H 2.37

Divinylthallium Chloride. Vinylmagnesium chloride was prepared from 7.2 g (0.3 mole) of magnesium and 60 g (1 mole) of vinyl chloride in 40 ml of tetrahydrofuran (reflux condenser, and under cooling with a mixture of acetone and solid CO_2). An ethereal solution of 45 g (0.15 mole) of $TlCl_3$ was added dropwise to the Grignard reagent at 5-10°. The reaction product was decomposed with 3% HCl solution. The product, amounting to 24 g (57%), was an infusible powder, which was crystallized from pyridine.

Found %: C 16.19; 16.24; H 2.04; 1.99 C_4H_6TlCl. Calculated 16.38; H 2.05

Divinylthallium Bromide. Reaction between 16.5 g (0.037 mole) of $TlBr_3$ and vinylmagnesium bromide prepared from 1.75 (0.07 mole) of magnesium and 8 g (0.07 mole) of vinyl bromide in tetrahydrofuran gave 6 g (45%) of a solid substance, which was crystallized from pyridine.

Found %: C 14.34; 14.33; H 2.08; 2.01 C_4H_6TlBr. Calculated %: 14.20; H 1.79

SUMMARY

1. Mono- and di-vinyl compounds of mercury and thallium and divinyl compounds of tin were synthesized.

2. An investigation was made of the reactions of divinylmercury with lithium, mercury salts, and thallium salts and also of the reactions of divinylthallium halides with mercury and with tin and thallium halides.

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* The atomic refraction of mercury in cis-cis-bis-2-chlorovinylmercury is 10.808 [11].

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MAGNETIC SUSCEPTIBILITY AND STRUCTURE OF NITROSYL COMPLEXES OF RUTHENIUM

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The work of Zviagintsev and Starostin [1] has shown that the nitrosyl complexes of ruthenium are exceptionally stable. They do not react with thiourea and mercaptobenzothiazole; the precipitation of ruthenium by reducing agents is slow; and oxidation, even by oxidizing agents such as dichromate and permanganate, is also very slow. The question of the character of the binding of the nitrosyl group in these complexes is of interest.

TABLE 1

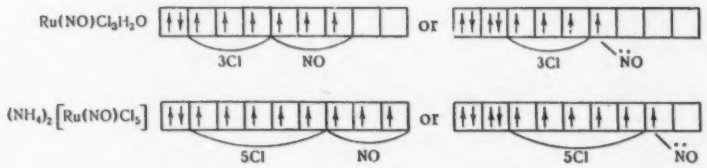
Magnetic Susceptibilities of Nitrosyl Compounds of Ruthenium

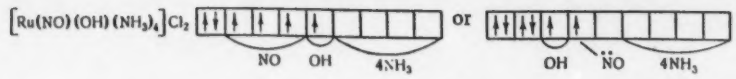
Formula of compound	Magnetic susceptibility	
	$\chi_g \cdot 10^6$	$\chi_{mole} \cdot 10^6$
$Ru(NO)Cl_3H_2O$	—0,207	—53
$(NH_4)_2[Ru(NO)Cl_5]$	—0,372	—128
$(NH_4)_2[Ru(NO)(OH)Cl_4]$	—0,388	—127
$[Ru(NO)(OH)(NH_3)_4]Cl_2$	—0,417	—120

We measured the magnetic susceptibility of four nitrosyl compounds. They were all found to be diamagnetic. The results of the measurements are given in the table.

The fundamental state of ruthenium is $4d^7\,5s\ (^5F)$. An optical transition into the $4d^6 5s5p(^7D_0)$ state requires about 72 kcal. In the case of iron the transition from the fundamental state $3d^6 4s^2(^5D)$-$3d^6 4s4p(^7D_0)$ requires about 54 kcal. In osmium such a transition requires 55-60 kcal.

The nitrosyl group may be attached to the central atom by a single bond of the type M—N=O. If the ruthenium is in the fundamental state, then in all the complexes investigated there remains an empty orbital after the formation of the bonds with the ligands and the single bond with the NO, and this empty orbital may form bonds with the unshared electron pair of the nitrogen. This corresponds to the state $^-M=^+N=O$. If the state of the central atom is d^6sp, then it is possible to have a triple bond with the nitrogen of the type $M\equiv{}^+N^-O$. All these states of equal total spin combine together. We consider it probable that in the bonds formed by nitrogen with oxygen and ruthenium atoms $2s^2 2p^3$ electrons of nitrogen take part. This can be shown diagrammatically as follows:





The reported data on other nitrosyl complexes of ruthenium which are also diamagnetic [2], are in accord with our views. This is true of the pentammines $[Ru(NH_3)_5(NO)]Cl_3 \cdot H_2O$ ($-\chi_{mole} \cdot 10^6 = 148$), of $[Ru(NH_3)_5(NO)]Br_3 \cdot H_2O$ ($-\chi_{mole} \cdot 10^6 = 169$), of $[Ru(NH_3)_5(NO)]SO_4(S_2O_6)_{1/2}$ ($-\chi_{mole} \cdot 10^6 = 100$) and of $K_2[Ru(NO_2)_4(NO)(OH)]$.

An x-ray structure investigation of $[Ru(NO)(OH)(NH_3)_4]Cl_2$ and $(NH_4)_2[Ru(NO)(OH)Cl_4]$ was carried out by Bokii and Parpiev [3]. The distance between the ruthenium atom and the ammonia nitrogen atom is 2.23A. On the other hand the distance between the ruthenium atom and the nitrosyl nitrogen atom is 2.07 A for the first compound and 2.03 A for the second. The extent of the reduction in the distance indicates that the bond is stronger than the bond formed with only unpaired electron of the nitrogen of NO and also than the bond formed with only the unshared pair of electrons of NH_3. In the case of the pure bond $M-N=O$, the angle formed at N must be 90-105°. In the case of bonds of the types $^{-}M^{+}N=O$ and $M\equiv{}^{+}N-{}^{-}O$ the angle must be 180°. Experiment gives about 150° and 153°. This indicates considerable participation of $2s^2$ electrons of nitrogen in the bond. We may point out also that the distance between the nitrogen atom of NH_3 and the oxygen atom of the nitrosyl group of a neighboring molecule is 2.78 A. This indicates the presence of a hydrogen bond between ammonia hydrogen and nitrosyl oxygen, which therefore has a considerable negative charge. It is of interest that the compound to which the formula $K_2[Ru(NO_2)_5]$ was ascribed is actually diamagnetic and has the composition $K_2[Ru(NO_2)_4(NO)(OH)]$ [4]. There is a reference in the literature [5] to the diamagnetism of $K_2[Os(NO_2)_5]$. However, such magnetic behavior is incompatible with a formula corresponding to one unpaired electron. We consider that this substance has the composition $K_2[Os(NO_2)_4(OH)(NO)]$.

In conclusion we express our thanks to V. N. Filimonova and N. A. Parpiev for making the compounds available to us.

SUMMARY

1. The magnetic susceptibilities of four nitrosyl complexes of ruthenium were measured. They were all found to be diamagnetic.

2. The observed diamagnetism is not incompatible with the view that the unshared electrons of nitrogen participate in the bonds between the metal and the nitrosyl group.

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A CASE OF SLOW HYDROGEN EXCHANGE IN THE >N–H GROUP

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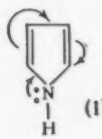
It is well known that there are two types of A–H groupings differing with respect to their behavior in the hydrogen-exchange reaction. O–H, N–H, Cl–H, Br–H, and I–H are of the first type. In these bonds the hydrogen atom undergoes instantaneous exchange with the deuterium of heavy water, alcohol, or ammonia. Hydrogen exchange is so rapid that it has not been possible to study its kinetics. Groupings of the other type include $-\overset{|}{\underset{|}{C}}-H$ and $-\overset{|}{\underset{|}{Si}}-H$. In these bonds hydrogen undergoes exchange with the deuterium of D_2O or C_2H_5OD generally only in presence of a catalyst or under the action of substituents that weaken the C–H bond. The kinetics of these reactions have been extensively studied.

This difference in the rates of hydrogen exchange cannot be explained on the view that the bond energy in compounds of the second type is less than in compounds of the first type. This will be seen for example, from the fact that the energy of the C–H bond is 87 kcal. whereas that of the O–H bond is 110 kcal. Brodskii drew attention to the fact that all atoms linked with H in groupings of the first type have a free pair of electrons, whereas $-\overset{|}{\underset{|}{C}}-$ and $-\overset{|}{\underset{|}{Si}}-$ have no free pairs [1]. Brodskii explained the role of free pairs in hydrogen-exchange reaction on the view that addition of D^+ and elimination of H^+ occur simultaneously in this case according to the scheme:

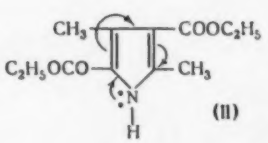
In contrast with this, because of the absence of a free electron pair on the atom attached to hydrogen in C–H bonds, exchange must be preceded by partial or complete elimination of a proton. What we have stated above can be regarded as an indication that reactions of the first type proceed with low activation energy, whereas those of the second type require a considerable activation energy. The correctness of Brodskii's explanation is now finding confirmation in extensive experimental investigation [2].

In the course of our investigations we encountered a fact which presented interest from the point of view of Brodskii's ideas, according to which a "free" electron pair results in instantaneous hydrogen exchange and its absence makes hydrogen exchange difficult. It might be expected that in pyrrole (I), in which the electron pair on the nitrogen is part of a unified conjugated aromatic system of six π-electrons (a closed system in Hückel's sense), i.e. is not altogether "free", the exchange of H in the N–H bond would proceed at a measurable rate.

A well known manifestation of the fact that the electron pair of the pyrrole nitrogen is not altogether "free" is the feebleness of the basic properties of pyrrole. It was indeed found that hydrogen exchange between D_2O and the N–H group of pyrrole in dioxane solution is slow. Thus, at 20° in 30 minutes, exchange proceeds to 40% of the extent calculated for exchange equilibrium.



(I)



(II)

It was found possible to measure the kinetics of this reaction. As an object for our kinetic measurements, we selected diethyl 3,5-dimethly-2,4-pyrroledicarboxylate (II), because of the readiness with which it was separated. Rate constants were calculated from a first-order equation. The experiments were carried out at 12°, 15°, 20°, and 25°. $K_{12} = 3.2 \cdot 10^{-5}$; $K_{15} = 5.6 \cdot 10^{-5}$; $K_{20} = 1.07 \cdot 10^{-4}$; $K_{25} = 2.21 \cdot 10^{-4}$ in sec^{-1}. The apparent activation energy was 25,500 cal.

EXPERIMENTAL

The performance of the experiments in dioxane solution made it possible to take test samples at times ranging from 5 minutes to 3 hours. The exact measurement of the kinetics was rendered difficult by the impossibility of separating the water and the substance instantaneously. Heavy water was removed with dioxane by vacuum distillation. The distillation required 1-5 minutes. The test samples were taken in two-necked flasks, and dioxane and water were distilled off under the vacuum of an oil pump with maintenance of the same temperature in the flask as that in the thermostat.

Diethyl 3,5-dimethly-2,4-pyrroledicarboxylate (2.00 g) and dry dioxane (75 ml) were introduced into the flask. When the whole of the substance had dissolved, the solution was placed in a thermostat, and 0.50 g of D_2O and 25 ml of dioxane were added.

SUMMARY

1. It was found that the isotopic exchange of the hydrogen of the NH group of diethyl 3,5-dimethly-2,4-pyrroledicarboxylate proceeds relatively slowly.

2. A study was made of the kinetics of this reaction at various temperatures.

3. The slow hydrogen exchange that occurs in this case is interpreted from the point of view of A. I. Brodskii's theory.

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SPECTROSCOPIC INVESTIGATION OF THE LOSS OF HYDROXY GROUPS OF CELLULOSE UNDER THE ACTION OF NITROGEN DIOXIDE

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The chemistry and mechanism of the oxidative reactions of cellulose are of importance in treatments of vegetable tissues andcellulose. The transformations of cellulose due to the oxidation of hydroxy groups constitute a very important process for the modification of the chemical properties of cellulose as a macromolecular substance [1]. However, the separate determination of the secondary and primary hydroxy groups participating in the reaction has not been worked out. The existing methods (tosylation, iodination, tritylation) possess all the defects of indirect methods [2]. Methods of determining hydroxy groups by the action of specific oxidizing agents are also unreliable because of occurrence of side reactions[3, 4].

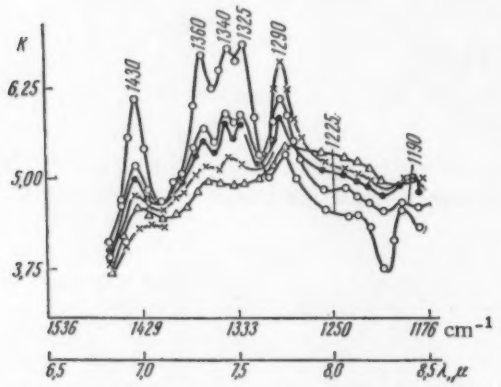


Fig. 1. Absorption spectra in the range 7-8.5 μ: o—unoxidized cellulose and products of the oxidation of cellulose with oxides of nitrogen and having the following COOH contents: o—7.6%; •—12%; x—16%; Δ—21%.

This paper reports an investigation on the transformations of the hydroxy groups of cellulose when it is oxidized with nitrogen dioxide vapor. The oxidation of cotton cellulose in the form of gauze was carried out under static conditions [5]. Products of reaction were washed out with water. To determine the change in the content of hydroxy groups in the course of the reaction we used infrared spectroscopy. The absorption spectra were determined on an IKS-11 recording infrared spectrograph with a rock salt prism by the method described previously [6].

In the spectra of cellulose materials the symmetrical valence vibration of hydrogen-bonded groups lies at 3330 cm^{-1}, and that of free hydroxy groups lies nearby at 3570 cm^{-1}. Fall in the intensity of absorption in these regions characterizes reduction in the total content of hydroxy groups. Absorption bands at 1360, 1340 and 1325 cm^{-1} correspond to the vibration of primary hydroxy groups, as in the case of alcohols [7]. An indirect method of determining the loss of hydroxy groups in cellulose is based on our observation [4] of the reduction in the intensity of the band at 1430 cm^{-1}, which corresponds to the internal deformational vibration of CH groups. The reduction in the total number of hydroxy groups in the course of the oxidation of cellulose with NO_2 was calculated from the fall in intensity of the absorption band at 3330 cm^{-1}. Fig. 1 shows a considerable fall in the intensities of the bands of the primary hydroxy groups at 1360, 1340, and 1325 cm^{-1} with increase in the degree of oxidation of the sample, which indicates oxidation of the hydroxy groups. Curve 1, Fig. 2. shows the relation of the loss of hydroxy groups to the accumulation of carboxy groups, as determined by the calcium acetate method. This curve shows that the loss in hydroxy groups is proportional to the gain in carboxy groups. Curve 2, Fig. 2, which was plotted from the spectrum data of Fig. 1, shows the loss in primary hydroxy groups in its relation to the gain in the number of carboxy groups in the products. The increase in the intensity of the band at 1290 cm^{-1}, which characterizes the accumulation of nitric ester groupings, will be considered separately.

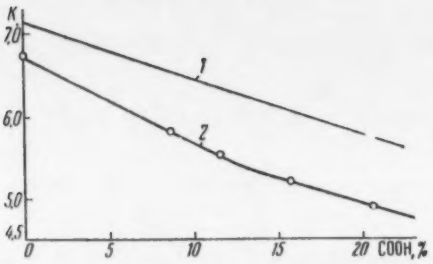
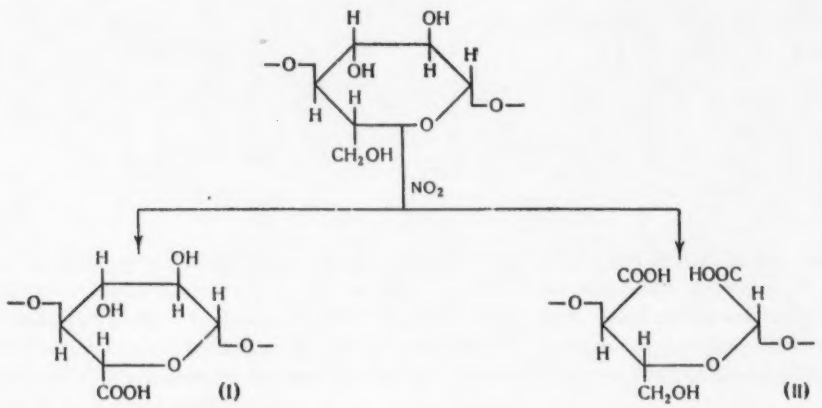


Fig. 2. Relation of loss of hydroxy groups, determined from spectrum data, to the accumulation of carboxy groups:
1) total hydroxy groups; 2) primary hydroxy groups.

When we compare the loss of primary hydroxy groups with total loss of hydroxy groups in the reaction for the formation of a given amount of carboxy groups, we find that, if we take the ratio of these losses as 1 at the beginning of the process, then at the end of the reaction it is 0.52. As will be seen from Curve 1, Fig. 2, the total loss of hydroxy groups corresponding to the formation of unit amount of carboxy groups remains approximately constant Hence, at the start of the process (until about 12% of COOH groups are formed) the formation of carboxy groups proceeds mainly at the expense of primary hydroxy groups (I). The rate at which they react then falls, and as the rate at which hydroxy groups of both kinds react scarcely changes, in the next stage the accumulation of carboxy groups must proceed also at the expense of secondary Hydroxy groups (II). Hence, uronic carboxyls are formed mainly in the early stages of the oxidation. This is again evidence of quasihomogeneous oxidation by oxides of nitrogen. If the reaction was heterogeneous, oxidation of primary and secondary hydroxy groups would be observed already in the early stages in the more accessible regions of the cellulose, working inward from the surface; and then, as the oxidizing agent diffused, the same process would be observed in the compact regions. Hence, in this case the primary factors are the differences in reactivity of the hydroxyls of cellulose and the specificity of the oxidizing agent, and the differences in the densities of packing of the different region of the cellulose have only secondary effects.

The process studied in this investigation may be represented as follows:



The results are in good agreement with those of investigations [1,4] in which it was shown by chemical methods that part of the carboxy groups are formed by oxidative cleavage of the pyran ring.

SUMMARY

1. The loss of hydroxy groups in the oxidation of cotton cellulose with nitrogen dioxide vapor was studied with the aid of infrared spectra.

2. The reaction is quasihomogeneous; in the first stage products are formed mainly by the oxidation of primary hydroxy groups, and in the second stage by the oxidation of primary and secondary hydroxy groups.

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ENERGY BARRIERS IN RING-OPENING AND RING-CLOSING REACTIONS OF HYDROCARBONS

G. I. Levi and A. A. Balandin

The reaction of hydrogenolysis of cyclic hydrocarbons with opening of the ring and of dehydrocyclization with formation of five-membered rings were studied in detail by Kazanskii and co-workers [1]. The height of the energy barrier E' for these reactions can be found from the equations of the multiplet theory [2]. The value

TABLE 1

	C_{al}	$C_{\triangle}$	$C_{\square}$	$C_{\overline{\cup}}$	C_{ar}	Pt	Pd	Ni
C_{al}	82,87					13,5	13,8	16,0
$C_{\triangle}$		73,8				28,8	30,3	31,8
$C_{\square}$			76,4			(23,7)		
$C_{\overline{\cup}}$				81,67		(18,6)		
C_{ar}					112,0	39,7	—	43,8
H	98,75				108,1	54,2	53,3	50,1

of E' is found as the difference of the energies of the bonds that are broken and formed in any stage of reaction which is a limiting stage. In the given case we consider that this is the adsorption stage, i.e. the stage of formation of the multiplet complex. The lower the absolute value of E', then, other conditions being equal, the more readily will the reaction occur: the lower will be the temperature at which the reaction will occur (as compared with another reaction with a higher energy barrier), or the higher will be the yield of reaction products if the comparison is made at a given temperature.

Hydrogenolysis of a C–C Bond with Ring-opening. Let us find the height of the energy barrier of the adsorption stage of the hydrogenolysis reaction, proceeding on platinum by the doublet mechanism:

$$E' = -Q_{C-C} - Q_{H-H} + 2Q_{Pt-H} + 2Q_{Pt-C}.$$

Here Q is the energy of the bond indicated by the subscript; the values are taken from the papers [3-5] and are given in Table 1 in kcal. The subscripts attached to the letter C indicate the compounds in which the carbon atom occurs, and the values given in parentheses are obtained on the assumption that, in the transition from Q_{Pt-Cal} to $Q_{Pt-C_{ar}}$, Q varies in a regular manner.

Table 2 gives the results of the calculation of E' and the experimental data. The catalyst was platinized charcoal; apart from temperature, the conditions were the same in all cases [1].

It will be seen from Table 2, that, as required by theory, the difficulty of opening carbon rings increases as the absolute value of E' increases. From the relationship $\epsilon_{act} = -3/4 \cdot E'$ for the hydrogenolysis of cyclopentane we obtain $\epsilon_{act} = 30$ kcal. If we consider that in the formation of the multiplet complex there first occurs the cleavage of bonds in the ring, then in the calculation of E' we must use the value of Q_{Pt-Cal}. The sequence

of the heights of the energy barriers then remains the same, but the absolute values of E' increase. In this case for the hydrogenolysis of cyclopentane we obtain $E' = -50.5$ kcal and $\epsilon_{act} = 37.9$ kcal. In reality, of course, the deformation and weakening of the C–C and H–H bonds and the formation of bonds of the C and H atoms with platinum proceed simultaneously. It is interesting that the average of the values of the activation energy ϵ given above is 34 kcal, whereas the experimental value ϵ_{act}(expt) is 35 kcal [6].

TABLE 2

	T (°C)	Conversion (%)	−E' (kcal)
Opening of 3-membered ring (ethylcyclopropane)	50	100	12.0
Opening of 4-membered ring (methylcyclobutane)	250	83	~25
Opening of 5-membered ring (cyclopentane)	250	3	~40

If on the other hand, starting with the experimental value of the activation energy, we find the bond energy $Q_{Pt\text{-}C_{\square}}$, we may estimate the error which we have made as a result of our assumption of a uniform reduction in bond energy with increase in the number of carbon atoms in the ring. In accordance with [5], for the case of the hydrogenolysis of cyclopentane we shall have

$$Q_{Pt-C_{\square}} = \frac{1}{2}(Q_{C_{\square}-C_{\square}} - Q_{H-H}) - Q_{Pt-H} - \frac{2}{3}\epsilon_{act.\ (expt)}.$$

Whence $Q_{Pt\text{-}C_{\square}} \cong 15.5$ kcal, whereas with the assumption referred to above we obtained 18.6 kcal.

Dehydrocyclization with Formation of a Cyclopentane Ring. For the doublet reaction of dehydrocyclization of paraffins on Pt:

$$E' = -2Q_{C-H} + 2Q_{Pt-H} + 2Q_{Pt-C_{al}} = -62{,}1 \text{ kcal}.$$

For other catalysts we obtain: for Pd $E' = -63.3$ kcal, and for Ni $E' = -65.3$ kcal; i. e. the readiness with which cyclization occurs falls in the order Pt>Pd>Ni.* In passage from aliphatic to aliphatic-aromatic hydrocarbons, i. e. on replacement in the calculation of $Q_{H\text{-}C_{al}}$ and $Q_{Pt\text{-}C_{al}}$ by $Q_{H\text{-}C_{ar}}$ and $Q_{Pt\text{-}C_{ar}}$, the absolute value of E' should fall. Let us now compare these results with the experimental data. Experiment shows [1] that at 310° the cyclization of paraffins to cyclopentanes proceeds only on a Pt catalyst, but not over Pd or Ni; also, depending on the structure of the original substance, the yield varies from 7% to 30%. For aliphatic-aromatic hydrocarbons only the dehydrocyclization of propylbenzene has been studied; under the same conditions it proceeds to an extent of 6% [7]. The authors explain the lowness of the yield obtained in this case on the view that the reaction is probably inhibited by the powerful adsorption of benzene rings on platinum [6].

Hence, the results of calculation are in accord with experiment. It should be noted that the differences between the heights of the energy barriers are very small. This gives us reason to consider that Pd and Ni do not bring about the closing of a five-membered ring not only because of energetic difficulties, but also for various other reasons (inadequate geometric correspondence, adsorption peculiarities, etc.). The examples examined above exhaust the whole of the experimental material on the catalytic transformation of hydrocarbons over metallic catalysts, as generalized in the article [1], with the exception of one case of greater complexity, namely

* This order should be preserved also when the quantity used in the calculation is not $Q_{M\text{-}C_{al}}$, but $Q_{M\text{-}C_{\square}}$ (which is as yet unknown); the absolute values of E' will then be lowered by at least 9-11 kcal (M = metal).

the reaction of hydrogen with isopropenylcyclopropane, in which the direct calculation of energy barriers is as yet impossible because of the absence of data for the basis of the calculation.

SUMMARY

1. Calculation from the equations of the multiplet theory of the heights of the energy barriers in reactions of hydrogenolysis of hydrocarbons with opening of 3-, 4-, and 5-membered rings and of dehydrocyclization with formation of a cyclopentane ring gives results that agree with the experimental data.

2. The value of the energy of the bond formed between a C atom of cyclopentane and a platinum catalyst was estimated.

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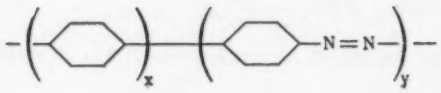
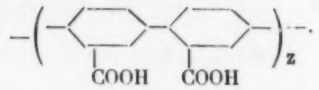
LETTERS TO THE EDITOR

Polynuclear aromatic compounds are distinguished by their high thermostability. In recent years much attention has been devoted to the synthesis of polyphenylenes.

We have synthesized compounds of this sort via aromatic bisdiazo compounds. When treated with cuprous compounds, bisdiazotized benzidine loses nitrogen with formation of an infusible nitrogenous polymer of probable structure



By the bisdiazotization of 4,4'-diamino-3,3'-bisphenyldicarboxylic acid and subsequent decomposition of the product by the method indicated above we obtained a soluble, infusible polymer 

which lost carbon dioxide when heated. Tough films could be prepared from its solutions. This polyacid opens up new possibilities for the synthesis both of the linear polyphenylenes themselves and of their derivatives.

Analogous transformations can be effected also via N,N'-diacetyl-N,N-dinitrosodiamines.

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RADICAL ADDITION OF HYDROGEN BROMIDE TO 1-BROMOACETYLENES

It was shown recently that the radical hydrobromination of substituted vinyl bromides proceeds by the trans-addition scheme [1, 2]. We obtained quite different results when we carried out this reaction in the acetylene series. The photochemical hydrobromination of 1-bromopropyne (I) and 1-bromo-3,3-dimethyl-1-butyne (II),

$$RC{\equiv}CBr + HBr \rightarrow RCBr = CHBr$$

proceeds stereospecifically and leads to products of the cis addition of hydrogen bromide, i. e. to trans-dibromo olefins. The reaction was carried out in the radiation of a quartz mercury lamp at −75° in absence of solvent or in a pentane medium. When the reaction was carried out in pentane, (I) gave a 92% yield of 1,2-dibromopropene, b.p. 63-65° (61 mm) and $n^{20}D$ 1.5302, and, judging from the infrared spectrum (x_{980} 4.40) this contained 75 ± 7.5% of the trans isomer. Pure trans-1,2-dibromopropene, synthesized by addition of bromine to propyne in propionic acid in presence of LiBr at −30°, had b.p. 46-47° (40 mm), $n^{20}D$ 1.5335, and x_{980} 5.8.

The analogous hydrobromination of (II) gave 1,1-dibromo-3,3-dimethly-1-butene (III) in 89% yield; b.p. 68-70° (16 mm); $n^{20}D$ 1.5171; containing, according to the infrared spectrum (x_{980} 0.56) 95 ± 5% of trans isomer. Pure trans-(III), synthesized by addition of bromine to 3,3-dimethylpropyne in acetic acid in presence of LiBr, has b.p. 68-69° (16 mm); $n^{20}D$ 1.5179; x_{980} 0.58. It was shown by special experiments that cis-(III) is not isomerized under the conditions of reaction; hence, the photochemical hydrobromination of bromoacetylenes is a radical reaction of cis addition.

L. D. Bergel'son

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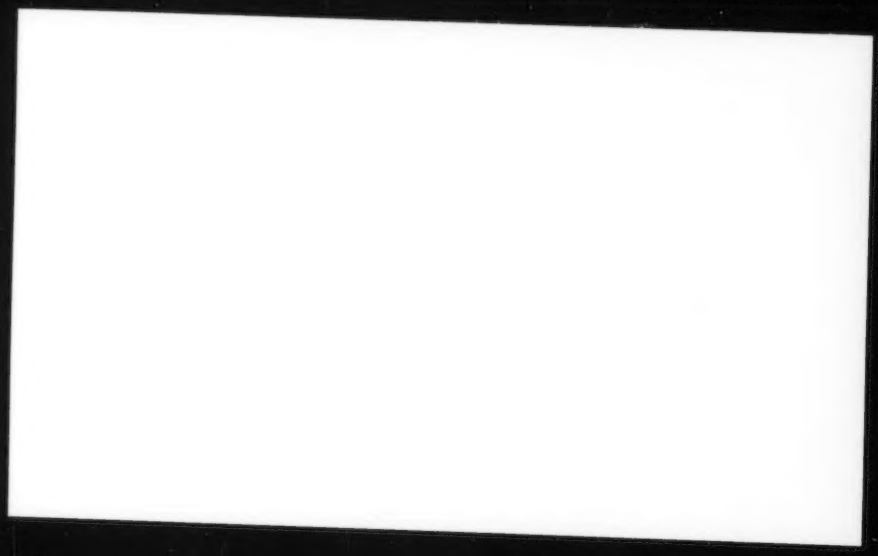

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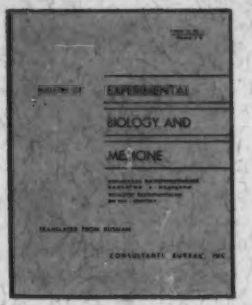

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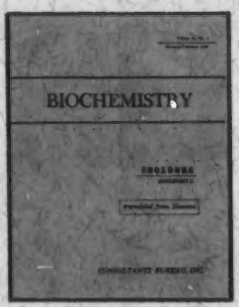

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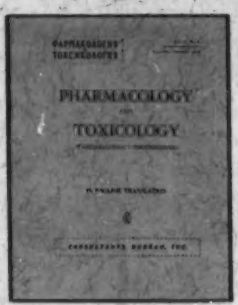

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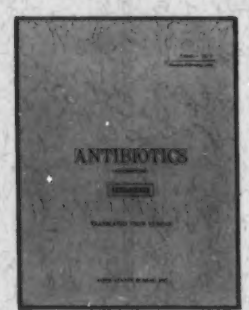

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